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POROUS TOOLING PROCESS FOR MANUFACTURE OF GRAPHITE/POLYIMIDE COMPOSITES

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DOWNEY, CALIFORNIA

CONTRACT NAS1-15501
JANUARY 1981

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FOREWORD

This is the final report on an effort to develop, demonstrate, and verify porous tooling techniques and processes for manufacture of graphite/polyimide composites. The program was conducted in accordance with the requirements and instructions of Contract NAS1-15501. Customary units were used for the original measurements and calculations. In this report, units are expressed in the International System of Units (SI) with English units in parenthesis.

The project engineers were L. W. Smiser, K. K. Orr, and S. M. Araujo.

Use of commercial products or names of manufacturers in this report does not constitute official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.

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SUMMARY

On curing, graphite/polyimide (Gr/PI) laminates evolve steam and other volatiles, which must be removed to prevent internal voids. Porous steel tools are effective in removing these volatiles but are costly and time-consuming to machine. Thus, there is a need for inexpensive, easily fabricated, porous tooling for the layup of large, curved sections of Gr/PI laminates. Porous, castable refractories appeared to be good candidates because they are low in cost and can be easily cast into any shape.

Four commercial castable refractories were characterized and tested as 12.7 x 12.7 cm. (5x5 in.) porous tools. Resco 17E was selected on the basis of permeability, mechanical strength, and performance as a porous tool for preparing PMR-15 laminates. Resco 17-E comprises a silicate aggregate bonded with an hydraulic cement system. Under similar conditions, the Resco 17-E tool outperformed steel caul plates in the number of plies of PMR-15 which could be molded without internal defects.

PMR-15 laminates measuring 30 by 30 cm. (12x12 in.) were prepared to fully demonstrate the effectiveness of Resco 17-E as a tool material. Unidirectional laminates of three thicknesses, up to 32 mm. (0.125 in.), were fabricated at three levels of mold permeability. In addition, one (0, +45, 90, -45)s laminate was prepared on the tool with the most promising results.

Laminates were characterized in regard to ultrasonic C-Scan flexural strength, interlaminar shear strength where possible, void content, and glass transition temperature. It was found that up to 14 plies of PMR-15, giving a unidirectional laminate thickness of 3.0 mm. (0.12 in.), could be laminated to give excellent mechanical properties with no apparent internal defects.

In future studies on porous tooling, it is recommended that the following areas be addressed.

1. Brittle materials, such as castable ceramics, require thick sections to reach load carrying capacity required in applications such as tooling for laminate curing. This increases the path through which reaction products must pass and reduces the effectiveness of the tool. Introduction of cylindrical holes near the center plane of the tool will shorten the paths, providing lower resistance pathways for volatiles. Such holes could be cast in or incorporated as a sacrificial phase or planned porosity. The former way allows placement at the cross-section location where they will allow a minimum strength loss such as on the neutral axis in the case of bending. Many ramifications of this idea can be pursued.

2. Further investigation of filler materials and how their size distribution and shape effects strength and permeability. Addition of strengthening fibers or wires should be included since they perform the same function as the aggregate, i.e., promoting strength, conductivity, etc. Stainless steel wire, graphite and other ceramic fibers and whiskers should also be considered viable strengthening materials.

SYMBOLS, UNITS, AND PARAMETERS

Angstom	10^{-10} meter
BTU	British thermal unit (1055 joule at 16°C)
C	Composite density
°C	Temperature, degrees Celcius
Centidarcy	A unit of permeability. One centidarcy equals a flow of 0.01 cm^3./sec. of a fluid of 1 centipose viscosity through a 1-cm. cube under a pressure differential of 0.10 megapascal (1 atmosphere).
cm.	Centimeter (10^{-2} meter)
$cm.^3$	Cubic centimeter
°F	Temperature, degrees Fahrenheit
F	Density of fiber (graphite)
F_s	Ultimate short beam shear strength
F_L	Ultimate longitudinal flexural strength
g.	Gram (mass)
Gr/PI	Graphite/Polyimide
HIMAT	Highly Maneuverable Aircraft Technology
hr.	Hour
in.	Inch
kg.	Kilogram
$kg./m.^3$	Kilogram per cubic meter
L	Length
lb.	Pound
$lb./ft^3$	Pound per cubic foot (16.018 $kg./m.^3$)
m.	Meter

M.	Modulus of rupture
mg.	Milligram (10^{-3} gram)
micrometers	10^{-6} meter
mil	One thousandth of an inch (0.00254 cm.)
min.	Minute
ml.	Milliliter (10^{-3} liter)
mm.	Millimeter (10^{-3} meter)
MPa	Megapascal (10^{6} pascal)
P	Maximum load carried by specimen
psi	lb./in.^{2} (0.0068948 megapascal)
R	Density of resin
S	Span (in flexural test)
t	Thickness
ton	909kg. (2000 lb.)
Vc	Void content (volume-percent)
W	Width
W_1, W_2, W_3	Weight, explained in Appendix B.4
W_F	Weight-percent of fiber
W_R	Weight-Percent of resin

1.0 INTRODUCTION

1.1 The Need for Porous Tooling

Graphite/polyimide (Gr/PI) laminates are capable of long-term service at 315°C (about 600°F). A typical use is for structures on the Space Shuttle Orbiter, allowing weight savings and lower thermal expansions in comparison to the present metallic and glass reinforced composites.

Gr/PI prepregs typically contain low-boiling aromatic solvents. These must be efficiently removed during B-staging, at 121-204°C (350-400°F), to obtain void-free laminates. During the imidization (cure) cycle at 204-260°C (400-500°F), the major reaction by-product, steam, is evolved. In the concluding (crosslinking) phase of the cure at 316-343°C (600-650°F), remnant solvents and by-products must be removed.

Standard fabrication techniques, using perforated steel caul plates and bleeder materials such as fiberglass cloth, succeed in preventing voids in thin laminates, up to 0.13 cm. (0.050 in.) in thickness. However, thicker laminates have a tendency to retain volatiles and develop voids. Cross-plied laminates retain more volatiles than unidirectional ones.

Another difficulty in removing volatiles in conventional molding is that excess resin flows from the laminates and clogs the bleeder material. In contrast, a porous tool would provide an infinite path for the escape of volatiles. Excess resin would be "blotted" by the tool surface.

The problem of removing volatiles is especially acute for curved tool surfaces, where methods such as the use of steel caul plates are impractical. Steel caul plates are expensive to machine, and their extended manufacturing time can delay production.

1.2 Requirements for a Porous Tool Material

Experience suggests the following requirements for porous tools:

(1) Air permeability of 0.047 centidarcy (2 ft.^{3}/min.ft.^{2} at a pressure differential of 14 psi for a thickness of one inch). Porosity must be homogenous over the tool surface.

(2) Modulus of rupture of 8.27 megapascals (1200 psi) at ambient temperature and 80% of this value at 343°C (650°F).

(3) Compressive strength of 20.7 megapascals (3000 psi) at ambient temperature and 80% of this value at 343°C (650°F).

(4) Linear thermal expansion coefficient close to that of Gr/PI laminates (2 to 9 x 10^{-6} cm./cm./°C).

(5) Adequate thermal conductivity for rapid and uniform heating/cooling of the tool during the cure process.

(6) Ease of fabrication

(7) Reasonable cost

(8) Reusability. Resin absorbed by the tool must be burned away periodically.

1.3 Castable Refractories as Materials for Porous Tooling

Porous metals are unsuitable candidates because of their high cost, while ablative foams lack adequate strength. The only materials which appeared likely to meet all the above requirements were castable refractories (high-durability ceramics) of controlled porosity.

As received, these materials are a blend of a relatively coarse aggregate, e.g. fused silica, and a finely-divided hydraulic cement, e.g. calcium aluminate. When water is added, the cement is hydrated, heat is evolved, and the aggregate particles are firmly bound together by amorphous gels.

Temperature resistance is high, e.g. 1650°C(3000°F). Porosity, hence permeability, is enhanced by firing. During firing the material loses its water of hydration and gains strength as a result of ceramic type bonding.

The pores, of course, must be interconnected to provide a continuous path. In essence, porous castables are dense, high-strength, refractory, open-celled foams.

The Tulsa Division of Rockwell International has used silica castables such as Fusil S-820 to construct large-area, thin-shelled tools for the lay-up of Gr/epoxy laminates (Figure 1). In this case, the surface was sealed to prevent parts from sticking to tool surfaces. Addition of stainless steel fibers was used to increase the bending strength by as much as eight times. (Reference 1). Steel fibers effectively strengthen various refractories (Reference 2). Beside providing reinforcement, they increase the thermal conductivity of the tool. Fusil S-820 was selected for its low-temperature cure (104°C, 220°F), its low coefficient of linear thermal expansion (0.8 x 10-6 cm./cm./°C), and its low cost ($1.21/kg, $0.55/lb.).

The Los Angeles Division of Rockwell International also utilized Fusil S-820 tooling for B-1 vertical stabilizer fabrication (Reference 3). Again, porosity was minimized rather than enhanced. The tool was a two-piece ceramic curing die (Figure 2) reinforced with Gr/epoxy stiffening rods. The rods were positioned while they were in a pliable, semi-cured state (B stage); they were then cured in position during the cure of the laminate. Carbon fibers (without epoxy) have been tested as reinforcements for cement as reviewed in Reference 4.

Reinforced tools for the Highly Maneuverable Aircraft Technology (HIMAT) project are shown in Figure 3.

The above experience provides a precedent for the use of tools made from castable refractories in fabricating graphite laminates. The object of the present work was to extend the application of castable refractories from nonporous tooling for Gr/epoxy laminates to porous tooling for Gr/PI laminates.

2.0 Screening of Castable Refractories for Porous Tooling

Five materials were studied. Three were castable refractories comprising premixed aggregate and hydraulic cement to which water is added before casting.

The fourth (Resco AA-22) was provided in two parts which were mixed before adding water. Evaluation of this material was suggested by Mr. Robert Baucom of NASA/LaRC. In this case, and acid (phosphate) bond is formed. The fifth material (Secar 71) was a pure calcium aluminate cement of the type incorporated in the first three materials.

The object of the study was to select the best candidate from among the four castable refractories in terms of (1) permeability, (2) modulus of rupture, (3) compressive strength, and (4) performance as a 12.7 x 12.7 x 2.5 cm. (5x5x1 in.) tool for curing Gr/PI laminate. As a first step, the properties of the uncured powders were reviewed. Then castings were prepared and properties were optimized in terms of the two controlling variables: level of water added, ("casting water") and the firing temperature. Next, Gr/PI laminates were prepared to judge the relative performance of the four castables as tools. Finally, the best candidate material was selected.

2.1 Properties of Castable Powders as Received

Manufacturers' data on aggregate composition, cement composition, total chemical analysis, particle size, and cost are given in Table 1.

In addition, a wet sieve analysis (Appendix A.1) was performed on the three hydraulic setting castables; results appear in Table 2. Presumably, the coarse material represents aggregate, while the fines (smaller than 325 mesh) represent the cement. The decrease in density on firing, in Table 2, correlates with the level of fines, supporting the correlation of fines with the cement phase. Fusil S-820 has the highest level of fines.

X-ray diffraction (Appendix A.2) indicated (Table 3) that Fusil S-820 fines was more crystalline than Thermo-Sil 120 or Resco RS-17E fines. Since all three of these materials gave the same diffraction pattern for the fines, this pattern presumably is due to the calcuim aluminate cement which is common to all three. Also, the fines (-325 mesh) were more crystalline than the course fraction (+80 mesh), except in RS 17E where the aggregate most closely resembles Sillimanite ($Al_2O_3.SiO_2$),

which is consistent with the conclusion drawn from fired densities, above that the fines represent the cement phase. Thus, the greater crystallinity of Fusil S-820 than Thermo-Sil 120 or RS-17E suggests more fines, and more cement in the Fusil S-820. Note that the $CaO+Al_2O_3$ content of Fusil S-820 is 37% according to the manufacturer (Table 1). This roughly corresponds to the 44% fines in Table 2.

The conclusion is that Thermo-Sil 120 and Fusil S-820 are both silica aggregate bonded with calcium aluminate cement, with the cement at a higher level in Fusil S-820. Resco RS-17E resembles Thermo-Sil 120 in cement content, but the aggregate (55% silica) is said to be the mullite type, probably sillimanite. Secar 71 is a calcium aluminate cement resembling the Alcoa CA-25 cement used in Thermo-Sil 120, Fusil S-820, and Resco 17-E.

2.2 Optimization of Properties after Casting and Firing

Data on castings provided by the manufacturers are given in Table 4.

Castings were prepared in accordance with each manufacturer's instructions; see Appendix C.1.

Results for density, water balance, permeability, modulus of rupture, compressive strength, and coefficient of linear thermal expansion are presented in Tables 4-9. The procedures for these test methods are given in Appendices A.3-A.6. Density and water balance were calculated from gravimetric data.

2.2.1 Properties vs. Water Added

As expected, both porosity, as judged by reduced density (Table 5), and permeability (Table 6) generally increased with the level of casting water. The explanation is that as more water is used to facilitate placement of the aggregate particles the resulting pore space becomes larger and the density decreases (Reference 5). Higher values for excess water also resulted (except for Resco AA-22) as the level of casting water was increased.

Also, as expected (Reference 5), the modulus of rupture tended to decrease significantly above a certain level of casting water (Table 7). The same was true for compressive strength; in Table 8 the compressive strength for fired castables decreased with increasing casting water in all cases.

The coefficients of thermal expansion (Table 9) were in substantial agreement with the manufacturers' data (Table 4) and are in the general range of Gr/PI laminates as required for close-tolerance tooling. Thermal expansion, which is judged not to be a highly critical property, was not studied vs. level of casting water. In general it is controlled by the continuous solid phase and is assumed to be the same regardless of porosity.

The conclusion is that a compromise must be made in regard to the level of casting water. Enough water must be added to attain the needed castability and permeability while retaining sufficient mechanical strength.

2.2.2 Properties vs. Firing Temperature

The critical property of compressive strength, which must exceed 20.7 megapascals (3000 psi), was studied vs. both casting water level and firing temperature. In general (Table 7), an increase in firing temperature from 704°C (1300°F) to 1093°C (2000°F) caused a modest decrease in compressive strength for Thermo-Sil 120, Fusil S-820 and Resco RS-17E. Resco AA-22 on the other hand, showed a modest increase in strength. A firing temperature of 1371°C (2500°F) made no great change in the case of Fusil S-820 but significantly increased the strength of Resco AA-22 at 0.073 $cm.^3$ casting water/g. powder.

The conclusion is that 704°C (1300°F) is an adequate firing temperature. The Resco AA-22 easily exceeded the requirements for permeability and mechanical strength when fired at this temperature.

2.2.3 Permeability

Permeability increased considerably after firing (Table 6) as the result of dehydration (Reference 5). Note that the results in Table 6 are far above the level of 0.047 centidarcy judged to be required for porous tooling. For fired Resco AA-22, at 0.063-0.068 $cm.^3$ casting water/g. powder, the permeability was 8 or 9 times the required level and for fires Resco RS17E at 0.13 cm^3 casting water, the permeability was about five times the reference level.

Resco RS-17E and Resco AA-22 were superior to the other candidate materials in permeability as well as in modulus of rupture and compressive strength.

2.3 Properties of Graphite/Polyimide Laminates Using Tools Made from Castable Refractories

Eight through 16 plies of unidirectional Gr/PI prepreg (PMR-15 Lot #2W 4461) were laid up and cured on perforated steel caul plates. Figure 5 shows the configuration. C-scanning (Appendix B-1 and Figure 6) indicated that up to 11 plies could be molded without defects. Therefore, an attempt was made to exceed this performance by molding 12 plies without defects using porous tooling. Tools were cast and laminates prepared as described in Appendices C.1 and C.2.

Properties of the tools and laminates are presented in Table 10. In all cases the permeabilities were far above the prescribed minimum of 0.047 centidarcy. Acceptable C-scan results were obtained for four of the tools, three cast of Resco RS-17E and one of Resco AA-22. All these successful tools had smooth surfaces.

Fracturing the surface of the ceramic tools after lamination revealed that resin had been deposited in the pores of the tools as shown in Figure 9. This substantiates the desired "blotting" effect of the tool in absorbing excess resin.

2.3 Properties of Graphite/Polyimide Laminates Using Tools Made From Castable Refractories

Firing the tools at 538°C (1000°F) for 4 hours completely evaporated the absorbed resin, thus suggesting reusability.

Resco AA-22 was presumed the best candidate on the basis of permeability and strength as well as the defect-free 12-ply laminate obtained when the tool surface was smooth (Table 10). Therefore, only Resco AA-22 tools were used for trial of the three lay-up configurations (A, B, and C) of Figure 10. Appendix C.2 gives the curing procedure. Twelve-ply laminates with clear C-scans resulted with configuration A, but 13-or 14-ply laminates were defective. Configuration C gave defect-free laminates with up to 13 plies but not 14. Only configuration B gave an essentially defect free 14-ply laminate, though defects appeared at 15 plies. Therefore, configuration B was preferred. Some relevant C-scans are shown in Figure 11.

The conclusion was that individual tool cavities (Figure 8) were unnecessary for the 12.7 x 12.7 x 2.5 cm. (5x5x1 in.) porous tools. With a flat steel tool and the preferred configuration B of Figure 10, defect-free laminates of up to 14 plies were prepared.

In the next experiment, Resco AA-22 tools and configuration B (Figure 10) again were used, but the tools had been fired at 982°C (1800°F), 1093°C (2000°F), and 1371° (2500°F) instead of the usual 704°C (1300°F). Again, laminates with clear C-scans were obtained for up to 14 plies. The conclusion was that the higher firing temperatures gave no significant improvement in tool performance.

Finally full size RS-17E tools 33x33x2.5-cm (13x13x1 inch), were cast to determine whether this tool material could produce laminates thicker than eleven plies with clear c-scans but using a second batch of PMR-15-pre preg which was lower in resin than the first lot. The three configurations shown in Figure 12 were used to produce five, nine, and fourteen ply laminates. Figure 13 shows the clear C-scans produced and Table 11 gives the physical characteristics determined from photomicrographs and density and thickness measurements upon data from gravimetric measurements. The agreement between photomicrographic fiber count and gravimetric measurement is very close as the data in Table 11 shows. (See Appendix B.4).

It has been the experience of this research group that different lots of PMR-15 prepregs require slight adjustments in vacuum and temperature of staging to make consistently good laminates from lot to lot of prepreg.

2.4 Selection of the Best Candidate Material for Porous Tooling

In strength and permeability, Resco AA-22 was the clear choice among the four castables tested. In the molding trials, however, RS-17E gave the best results and produced the most consistently

good laminates. Resco AA-22 was selected for further testing in the form of 12.7 x 12.7 cm (5x5 in.) porous tools, and it was found that defect-free laminates of up to 14 plies of PMR-15 could be prepared with the best of three layup configurations. Resco RS-17E was tested on a second lot (3W 1916) of PMR-15 and this lot produced good 14 ply laminates on both porous tools and on steel. In a control experiement with perforated steel caul plates instead of porous ceramic tools, using the first lot of prepreg (Appendix C.2, Figure 5), only 11 plies could be molded without defects.

Considerable difficulty was experienced when attempting to cast Resco AA-22 in 13x13x1 inch tools. Large voids were trapped in and near the working face of the tools and the low water contents required for adequate strength did not allow sufficient working time to produce the necessary smooth surface required for good laminates. RS-17E, on the other hand, was easily prepared in the larger size.

Nine 33x33x8.5 (13x13 in.) tools required by the contract was Resco RS-17E were cast and fired under the following conditions:

Casting water, 0.12-0.14 ^{3}/g. powder

Cured in mold at room temperature for 24 hrs.

Dried at 110°C (230°F) for 24 hrs.

Fired at 704°C (1300°F) for 1½ hrs.

3.0 Tooling Verification Study

In accordance with the contract, 30x30 cm. (12x12 in.) PMR-15 laminates were prepared. The porous tooling material was Resco RS-17E with casting water at 0.12, 0.13 and 0.14 cm. ^{3}/g powder.

3.1 Preparation of 30x30 cm. (12x12 in.) Graphite/Polyimide Laminates Using the Preferred Porous Tooling Material

The procedure for casting the Resco RS-17E mold is described in Appendix C.1. Unidirectional laminates of up to 22 plies of PMR-15 were prepared on tools of three different thicknesses. The cured thickness was F62, (0.30), 1.524 (.060) 3.040 (.120 in.). Duplicate panels and a (0, +45, 90, -45) panel were delivered to NASA-Langley. Photographs of these laminates are shown in Figure 12.

3.2 Characterization of 30x30 xm. (12x12 in.) Graphite/Polyimide Laminates

Typical C-scan results are shown in Figure 13. Clear scans were obtained for up to 22 plies of PMR-15.

Physical properties of the laminates, determined according to Appendices B.2-B.5 are summarized in Table 11.

(Properties will be discussed).

4.0 Conclusions

The 30x30 cm. (12x12 in.) Resco RS-17E tool was effective in the unidirectional lamination of up to 22 plies of PMR-15. Laminate thickness was 3.1mm. (0.122 in.)

In addition, a defect-free $(0, +45, 90\text{-}45)_5$ laminate was prepared successfully. It is concluded that Resco RS17-E, properly cast and fired, is an effective porous tooling material. With additional development of casting methods, Resco AA-22 could be equally acceptable for porous tooling.

5.0 Recommendation for Future Studies on Porous Tooling

In the use of castable ceramics, the design of load bearing parts must be approached by assuming that the material has no tensile strength and that where tensile loads are applied, reinforcement must be supplied in the form of supports or internal tensile members such as steel reinforcing rods to support such loads.

In order to vent away unwanted by-products of the cure of polyimide resins requires that there be a relatively low resistance path, however, this conflicts with the need for a relatively thick section for load carrying requirements. It is recommended that these problems of ceramic tool design should be thoroughly investigated, considering first the geometrical requirements dictated by strength, secondly the venting requirements for the removal of polyimide cure by-products.

Several possible solutions present themselves. First, a honeycomb like structure on the underside of the ceramic can provide the needed bending stiffeners and the reduced volatile escape paths. Second, the introduction of a porous layer just below the smooth tool face or a graded porosity through the thickness with the higher porosity near the tool face and decreasing with the thickness. This could be in the form of cast-in small diameter cylindrical holes near the tool face or as an incorporated sacrificial phase segregated in a layer near the tool face which burns out during an elevated temperature exposure.

Thermal properties and auxiliary internal heating must also be addressed. Any strengthening additions should also be a source of increased thermal conductivity. The cylindrical holes suggested above might also be a means of introducing internal tool heating to facilitate the curing process, especially if the tool has insufficient thermal conductivity for uniform heating. Any metallic reinforcement which might be considered for strengthening should also be considered for its effect on increasing thermal conductivity. Such materials as might be considered are stainless steel wire, graphite fibers, alumina or silicon carbide fibers. Addition of all of which can provide both increased mechanical strength and enhanced thermal conductivity.

Appendix Section A: Test Methods Applied to Castable Refractories

Appendix A.1

Wet Sieve Analysis

The method followed was ASTM C136-71. The N. B. S. mesh numbers in Tables 1 and 2 designate openings of the following sizes.

N.B.S. Mesh No.	Opening, Micrometers
4	4760
8	2380
10	1680
14	1410
20	841
30	595
40	420
70	210
100	149
140	105
200	74
325	44

Appendix A.2

X-Ray Diffraction

Course powders, e.g. (+80 mesh, were milled. Powders were mounted with a collodion binder. The instrument was a Siemens X-Ray Diffractometer, "Crystalloglex 4".

Appendix A.3

Permeability

Permeability was determined by ASTM C577-68. This method is intended for refractory brick and monoliths. The apparatus comprised a leak-proof system in which a 5.1 cm. (2 in.) cube was held in a pressurized rubber gasket. Means were provided for controlling gas pressure and measuring gas flow. Reference 6 describes the apparatus and presents permeability data obtained with it. Two silicone rubbers were tested as gasket materials. General Electric RTV 560 was too compressible to allow easy insertion of specimens and provide a good seal. However, the less-compressible RTV 577 allowed easy insertion of specimens and provided a good seal.

Permeability data are reported in units of centidarcys. Units of $ft.^3/min./ft.^2$ at a pressure gradient of 14 psi/in. are obtained by multiplying the value in centidarcys by 42.46.

Appendix A.4

Modulus of Rupture

The method was ASTM C78-75 for flexural strength using a simple beam with three-point loading. The modulus of rupture (M) in psi is calculated by:

$$M = \frac{(3)\ (\text{failing load, lb.})}{(2)\ (\text{width, in.})\ (\text{height, in.})^2}$$

The result is multiplied by 0.0068948 to convert to MPa (megapascals). Specimens 2.5x2.5x15 cm. (1x1x6 in.) were tested on an Tinius Olsen testing machine at a rate of loading of 0.23 cm./min. (0.09 in./min.).

Appendix A.5

Compressive Strength

Compressive strength was determined according to ASTM C116-68, using portions of broken beams from the modulus of rupture test. A Tinius Olsen testing machine was used, at a rate of loading of 0.13 cm./min. . Care was taken to keep the steel plates, between which the specimen was crushed, very nearly parallel so that the specimen was loaded evenly and fractured near the middle and not at a corner.

Since the specimens were 1x1 in. (2.5x2.5 cm.) in cross section, crushed between 1x1 in. plates, the crushing load in lb. was numerically equal to the compressive strength in psi. This result was multiplied by 0.0068948 to covert to megapascals.

Appendix A.6

Coefficient of Linear Thermal Expansion

The method was ASTM E228. This procedure uses a push-rod dilatometer to plot the expansion of the sample vs. increasing temperature.

Appendix Section B; Test Methods Applied to Graphite/Polyimide/Laminates

Appendix B.1

C-Scan Procedure

The instrument was an Ultrasonic C-Scan System comprising a US640 Series Scanning Bridge and associated equipment, manufactured by Sperry Division of Automation Industries, Chatsworth, CA. Reference 7 illustrates the application of this procedure to Gr/PI laminates.

The laminate under test was immersed in water, and an ultrasonic beam was passed through the specimen twice by means of a reflector. Scattering of the beam disclosed defects. Typical scans are shown in Figure 6 and 11. Defects indicated by this method include delamination, porosity, heterogeneities in fiber orientation, and blisters.

Appendix B.2

Flexural Strength

Conditions of the test were in accordance with Federal Test Method Standard No. 406, Method 1031. The specimen (Figure 14) was loaded to failure at 0.13 cm. (0.050 in.) per minute crosshead speed on a testing machine.

A mean value based on a minimum of three determinations was reported for longitudinal flexural strength using the formula below:

$$F_L = \frac{3PS}{2\ Wt^2}$$

Where: F_L = Ultimate longitudinal flexural strength, psi

P = Maximum load carried by the specimen, lb.

S = Span, in.

W = Specimen width, in.

t = Specimen thickness, in.

The result in psi is multiplied by 0.0068948 to convert to megapascals.

Appendix B.3

Interlaminar Shear Strength

The specimen (Figure 15) was loaded to failure at 0.13 cm (0.050 in.) per minute crosshead speed on a testing machine. The specimen was loaded as shown in Figure 15 with the smooth side up.

A mean value based on a minimum of five determinations was reported for short beam shear strength (interlaminar shear strength) using the formula below:

$$F = \frac{3P}{4\ Wt^{2}}$$

where: F_S = Ultimate short beam shear strength, psi

P = Maximum load carried by specimen, lb.

W = Specimen width, in.

t = Specimen thicknesses, in.

The result in psi is multiplied by 0.0068948 to convert to megapascals.

Appendix B.4

Void Content

The void content was calculated from resin/fiber content determinations. A mean value based on three determinations was reported. The calculation is:

$$V_C = 100 - \frac{W_F\ C}{F} + \frac{W_R\ C}{R}$$

where: V_C = Void content, volume-percent

W_F = Weight-percent of fiber

W_R = Weight-percent of resin

C = Composite density

R = Density of resin

F = Density of fiber

The fiber content was determined by acid/peroxide digestion of the cured laminate as follows:

Test specimens were approximately 1.27 cm x 1.27 cm. (0.5 in. x 0.5 in.) by laminate thickness. The test specimen was weighed to the nearest 0.1 mg (W_1) and placed in a 300 ml. tallform beaker, then 20 ml. of concentrated sulfric acid was added. The beaker was heated on a hot plate until fumes were evolved.

When the composite was visibly disintegrated and resin particles and fibers were dispersed throughout the liquid, hydrogen peroxide (50% concentration) was added dropwise down the side of the beaker. Rubber gloves and a fume hood with appropriate safety glass shield were used throughout the addition, and precautions were taken as recommended by the applicable safety regulations and procedures for handling hydrogen peroxide.

The reaction was considered complete when the hot sulfric acid solution below the fibers became clear and colorless. At this point, two more ml. of hydrogen peroxide was added to the solution, which was heated to evolve fumes for another 10 minutes to ensure complete decomposition of the polymer. The beaker was removed from the hot plate, allowed to cool to 21-27°C (70-80°F) and then placed in an ice bath.

Fibers were collected by vacuum filtration through a medium-porosity, sintered-glass crucible that had been weighed to the nearest mg. (W_2). After the sulfric acid had been filtered off, the fibers were washed in the crucible thoroughly with 600 ml. of distilled water added a few millileters at a time.

The crucible was removed from the filtering system and placed in an open beaker in an oven at 149°C (300°F) for 45 minutes. After drying, the crucible was cooled in a desiccator and weighed (W_3).

The resin and fiber content were calculated according to the following equations:

$$\text{Resin content, percent by weight } (W_R) = \frac{W_1 - (W_3 - W_2)}{W_1} \times 100.$$

$$\text{Fiber content, percent by weight } (W_F) = \frac{W_3 - W_2}{W_1} \times 100$$

Appendix B.4

Gravimetric and Photomicrographic Measurement of Thickness and Fiber Volume

Gravimetric data were taken on buttons of laminate cut with a one inch outside diameter diamond core drill at the thickest and thinnest points measured on the laminates. The specimens were weighed in air and suspended in water

and the difference divided by the density of water yields the sample volume. The diameters of the samples were nearly all 2.40 cm. (0.910 inch) using these diameter weigh data the laminate densities p_L and ply thicknesses t_p were calculated according to:

(p = rho)

$$p_L = \frac{W_d \, p_w}{(W_d - W_s)} \quad (8/cm^3) \qquad \text{and,}$$

$$t_p = \frac{(W_d - W_s)}{p_w} \quad \frac{(4)}{\pi \, (0.91)^2} = 1.5375 \, \frac{(W_d - W_s)}{p_w}$$

where:

W_d = dry sample weight

W_s = suspended sample weight

p_w = density of water

Photo micrographic data were taken directly from photo micrographs of a cross section of the laminate mounted in thermo setting plastic mounting media ground and polished and .05 micron alumina. Magnifications used was 3283 x and an average fiber diameter of 7.1×10^{-6}m (0.28×10^{-3} in.) was used in calculation of fiber volumes. A strip of the photomicrograph two centimeters wide the complete thickness of the section was counted. Only a fiber fill within the band was covered. Figure 19 shows a typical five-ply laminate cross section used. The section is void free, has a thin skin of cured resin on both faces and four resin rich bands separating the five individual plies with some blending of plies. Surface irregularities are caused by contact with TLL, a teflon coated glass fabric. Data are recorded in Table 11. Calculations of fiber volume and density are as follows:

$$V_f = 1.98 \times 10^{-7} \quad \frac{NM^2}{L}$$

where:

N = number of fiber ends in area 2 in. x L on photo micrograph

M = Magnification factor of the photo

L = Thickness of laminate on the photo

and

$$P_L = (P_f - P_r)\, V_f + P_r = 0.432\, V_f + 1.328 \quad (C.4.2)$$

where: P_f = fiber density (g/cm^3) = 1.670

P_r = cured resin density (g/cm^3) = 1.328

V_t = fiber volume fraction determined by (C.4.1.)

Appendix B.5

Glass Transition Temperature

The glass transition temperature (Tg), was determined as follows;

> A 0.64 x 0.64 cm. (0.25 x 0.25 in.) specimen was placed on the stage of a duPont 990 Thermomechanical Analyzer. The analyzer probe was weighted with approximately 5 g. and placed in contact with the sample. Heat was then gradually applied to the system. Probe displacement was monitored as the sample expanded upon the application of heat. The temperature at which the expansion curve for the sample changed slope was recorded as the glass transition temperature.

Appendix Section C: Procedures for Preparing Porous Tools and Graphite/ Polyimide Laminates

Appendix C.1

Preparation of Cast Refractory Test Specimens and Tools

The manufacturers' recommended procedures were followed for blending with water and curing:

> For example, equal weights of Parts A and B of Resco AA-22 were dry-blended using a Model N-50 Hobart mixer with a stainless steel bowl. Then the powder was removed from the bowl, 0.063-0.073 $cm.^3$ of water/ g. powder was added to the bowl, the powder was returned to the bowl the powder was returned to the bowl in several portions and the putty was blended thoroughly. After transfer to the mold, the material was allowed to stand at room temperature for 24 hours. Then the casting was removed from the mold and dried in a circulating-air oven at 100°C (212°F) for 1.5 hours. One-component powders were also dry-blended, prior to adding to the casting water, to ensure homogeneity. Firing was done with a Cress Electric Furnace, Model AG1536, at various temperatures from 627°C (1160°F to 1371°C (2500°F) for 1.5 - 2 hr.

In the preliminary study, three molds were used: a 5.1 cm. (2 in.) cube mold for permeability specimens, a 2.5x2.5x13.2 cm. (1x1x6 in.) bar mold for modulus specimens (fragments tested for compressive strength, and a 12.7x12.7x2.5 cm. (5x5x1 in.) mold with 0.64 cm. (0.25 in.) radii at the corners for the tools to prepare 12.7x12.7 cm. laminates.

All molds were of aluminum with a teflon coating. A surfacant solution (Trycol NP-9), Emery Industries) was applied as a mold release.

Tools of RS-17E cast in aluminum molds with 1/2 inch thick clear plastic faces. A schematic of the tool assembly is shown in Figure 16. The face plates and core were washed with a wetting solution of water and trycol NP.9[1] and clamped to the aluminum core. The mixture of cement and water was then poured into the open top and sealed with a plastic sheet and taped to prevent loss of moisture during the twenty-four hour ambient cure. Next, the tool was removed from the mold, air-dried twenty-four hours and then oven dried at 110°C (230°F) for twenty-four hours. The final preparation was a firing at 704°C (1300°F) for one and one-half hours.

Water contents of 0.12, 0.13 and 0.14 cm^3 per gram of powder were used in making tools of three different permeabilities as required by the contract.

Appendix C.2

Preparation of 12.7x12.7 cm. (5x5 in.) Graphite/Polyimide Laminates

The materials used were:

Kapton film, Type H, 0.51 or 0.76 mm (2 or 3 mils) (duPont)
Fiberglass breather cloth 120 or 162 weave (Thalco, Hess and Goldsmith, or other manufacturers)
Perforated caul plate, steel 1.6 mm. (1/16 in. (thick, with 1.5 mm. (0.060 in.) holes on 2.54 cm. (1.00 in.) centers.
Porous glass/Teflon separator film, style 3 TLL (Connecticut Hard Rubber). TX1040 (Pallflex Corporation) is a similar product.
Nonporous glass/teflon film, style 5TB (Connecticut Hard Rubber) Celgard, polypropylene film allowing one-way passage of vapor while excluding resin (Celanese Corp.)
Sealant A-800 (General Sealants, Inc.)
Celion 6000/PMR-15 unidirectional prepreg tape, cut to 12.7x12.7 cm. (5x5 in) or 30x30 cm. (12x12 in.) (U. S. Polymeric). This material was laid up in a unidirectional manner for alll the 30x30 cm. laminates. One (1) (0, +45, 90, -45)s 30 x 30 cm. laminate was prepared.

The layup was first prestaged in an oven and then cured in an autoclave. During cure in the autoclave the cycles were as follows:

Oven Prestage:
- Apply 25 cm.(10) Hg vacuum.
- Heat laminate to 218°C (425°F) at 5.6°C (10°F)/min. and hold for 30 min.
- Cool to 66°C (150°F) before relieving vacuum and removing assembly from oven.

Autoclave Cure:
- Apply full vacuum and 2.07 megapascals (200 psi).
- Heat to 249°C (625°F) at 1.6°C(3°F)/min. over 50 min.
  Hold 3 hr.
- Cool at 1.5°C (3°F)/min. to 149°C(300°F) over 2 hr.
- Cool at 3.3°C (6°F)/min. to 66°C (151°F) over 25 min. and release pressure and vacuum
- Cool at 3.4°C (6°F)/min. to 32°C (90°F) over 10 min. and remove laminate.

For molding with steel caul plate rather than ceramic tools, the configuration shown in Figure 5 was used.

Four different lay-up configurations were used with the porous tools: the one shown in Figure 8, and those shown in A, B, and C of Figure 10.

The first set of 12-ply laminates using porous tools (see Table 10) were laid up according to the configuration shown in Figure 8.

The screening tool holder (Figure 4) held fifteen 12.7x12.7x2.5 cm. (5x5x1 in.) tools. A detail, in cross section, for one of the tool cavities is shown in Figure 7. External piping was provided for drawing vacuum.

Additional sets of laminates with 12 or more plies were laid up in the three configurations (A, B, and C) of Figure 10 for the curing (autoclave) step. Note that the aluminum tool was replaced by a flat steel tool. In the pre-staging (oven) step, perforated steel caul plates were used instead of the steel tool indicated in Figure 10.

Appendix C.3

Preparation of 30x30 cm. (12x12 in.) Graphite/Polyimide Laminates

(The method was essentially that of Appendix C.2, using configuration A of Figure 10).

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3. M. S. Loyd, "Nonmetallic Castable Tooling for Advanced Composites", Rockwell International, Internal Report NA-77-312 (1977). (On request)

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COMPOSITION					
MATERIAL	MANUFACTURER	AGGREGATE	HYDRAULIC CEMENT	PARTICLE SIZE DATA	COST $/kg.-($/lb.)
Thermo-Sil 120	Thermo Materials Corp., Atlanta, GA.	Fused silica (over 90% SiO_2)	Calcium Aluminates (Alcoa CA-25)	-	1.21 (0.55), for 1-20 tons
Fusil S-820	Harbison-Walker Refractories Div., Dresser Industries, Inc., Pittsburg, PA.	Fused silica (99.5% SiO_2, 98% amorphous by X-ray diffraction). Total powder: 63% SiO_2, 8% CaO, 29% Al_2O_3	Calcium Aluminates (Alcoa CA-25)	N.B.S. Mesh No. / Cumulative % Retained: 10 / 0-4; 14 / 5-25; 30 / 35-51; 100 / 52-76; 200 / 83-100; 270 / 96-100	0.84 (0.38), for 1 ton or less
Resco RS-17E	Resco Products, Inc., Norristown, PA.	"Mullite type" (Mullite is 72% Al_2O_3, 28% SiO_2) Total Powder: 55% Al_2O_3, 35% SiO_2 1% Fe as Fe_2O_3, 6.3% CaO, 0.2% Mgo, 0.8% TiO_2, 1.1% alkali.	Calcium Aluminates (Alcoa CA-25)	N.B.S. Mesh No. / Cumulative % Retained: 4 / 0; 8 / 3; 20 / 43; 40 / 68; 100 / 82	0.42 (0.19). for less than 1/4 ton.
Resco AA-22	Resco Products, Inc., Norristown, PA.	Blend of accurately sized alumina aggregates (94-95% Al_2O_3, less than 0.2% SiO_2)	Acid-bonded by patented system. A minimum of 316°C (600°F) is used to stabilize the phosphate bond.	N.B.S. Mesh No. / Cumulative % Retained: 8 / 0; 14 / 9; 20 / 19; 40 / 43; 100 / 53; 200 / 57	0.97 (0.44), for less than 1/4 ton.

TABLE 1

Manufacturer's Data on Castable Refractory Powders

COMPOSITION					
MATERIAL	MANUFACTURER	AGGREGATE	HYDRAULIC CEMENT	PARTICLE SIZE DATA	$/kg. - ($/lb.)
Secar 71 (formerly Secar 250)	Lone Star Lafarge, Inc., Norfolk, VA.	None	Calcium Aluminates. Typical: 70.8% Al_2O_3, 27.2% CaO, 0.30% SiO_2, 0.25% Fe_2O_3, 0.5% MgO	60% less than 30 micrometers	0.38 (0.17), for 2-8 tons

TABLE 1 (cont.)

TABLE 2.

WET SIEVE ANALYSES OF CASTABLE REFRACTORY POWDERS

N.B.S. MESH NUMBERS or Property	WEIGHT PERCENT RETAINED					
	Fusil S-820		Thermosil 120		Resco RS-17E	
	TOTAL	+325 mesh only	TOTAL	+325 mesh only	TOTAL	+325 mesh only
+ 40	37.70	67.20	42.45	64.66	39.5	58.29
- 40 + 70	3.25	5.79	6.40	9.75	15.9	23.43
- 70 +100	1.25	2.23	4.35	6.63	4.3	6.34
-100 +140	2.50	4.46	3.60	5.45	4.6	6.78
-140 +200	5.65	10.07	3.25	4.95	2.1	3.10
-200 +325	5.75	10.25	4.85	7.39	1.4	2.06
-325	43.9	-----	35.10	------	32.2	-----
Aggregate Composition	Fused Silica		Fused Silica		Mullite Type	
Density as Cast kg/m^3 (lb/ft^3)	1855 to 1918 (116 to 120)		1839 to 1940 (115 to 121)		2099 to 2217 (131 to 138)	
Density after Firing at 627°C (1160°F) $kg./m^3$ ($lb./ft.^3$)	1746 (109)		1762 (110)		2019 (126)	
% Decrease in Density Caused by Firing	6.3		4.7		4.8	

TABLE 3.

X-Ray Diffraction Data on Castable Refractory Powders

MATERIAL	ANGLE (2θ)	APPROX. RELATIVE INTENSITY (PEAK AREA)	d (SPACING BETWEEN PLANES), ANGSTROM
Thermo-Sil 120, Fusil S-820, Fines	17.0	9	5.22
	23.4	10	3.80
	30.7	3	2.91
	36.2	2	2.48
	38.1	1.5	2.63
	44.0	1	2.06
PS17E Coarse Fraction	26.9	10	3.31*
	33.8	4.4	2.65
	40.4	3	2.23
	41.8	8	2.16
	43.1	36	2.09
(Fusil S-820 was more crystalline than Thermo-Sil 120 or Resco RS-17E)			
Resco AA-22 Part A or Part B	23.4	10	3.80
	26.6	1	3.35
	36,1	2	2.49
	38.8	1	2.32
	44.4	2	2.04
	53.6	1.5	1.71
	58.5	9	1.58

* Peaks Not Observed in Fines

TABLE 4. Manufacturer's Data on Cast Refractories

Material	Maximum Service Temperature, °C(°F)	Density kg./m.^{3} (lb./ft.^{3})	Porosity, %, at 540°C (1000°F)	Cold Crushing Strength, MPa (psi)	Modulus of Rupture MPa (psi)	Thermal Conductivity K Factor Kcal./m. m./hr./°C (BTU/in. ft.^{2}/hr./°F	Coefficient of Linear Thermal Expansion 10^{-6} cm/cm/°C (10^{-6}/in./in/°F	Linear Shrinkage, % after drying at 104°C (220°F
Thermo-Sil 120	1649 (3000)	1856-1890 (116-118)	-	6.89-41.4 (1000-6000) cured at 121°C (250°F)	6.89-10.3 (1000-1500) cured at 121°C (250°C)	0.53 (4.3) at 260°C (5000°F)	0.8 (0.45) at 0-1010°C (32-1850°F	Less than 0.1 when cured at 121 (250°F
Fusil S-820	1371 (2500)	1810(113) after curing at 104°C(220°F)/5 hrs, 1762 (110) after firing at 1093°C (2000°F)	-	48.3 (7000), cured at 104°C (200°F). 34.5 (5000) after firing at 1093°C 2000°F)	-	0.61 (4.95) at 538°C (1000°F)	-	Less than 0.2 when cured at 104°C (200°F for 5 hr.
Resco RS-17E	1510 (2750)	2083 (130)	25	48.3-68.9 (7000-10,000) at 1510°C (2750°F)	11.0-13.8 (1600-2000) at 1510°C (2750°F)	0.57 (4.60) at 260°C (500°F)	7.4 (4.1) at 21-1177°C (70-2150°F)	Less than 0.1 during cure.
Resco AA-22	1649 (3000)	2643 (165)	22	96.5-110.3 (14,000-16,000) at 1649°C (3000°F	-	1.25 (10.20) at 260°C (500°F)	11.5 (6.4) at 21-982°C (70-1800°F)	Less than 0.1 during cure.
Secar 71 (formerly Secar 250)	1816 (3300)	Properties depend upon aggregate						

TABLE 5. DENSITY AND WATER BALANCE OF CAST REFRACTORIES

Material	Casting Water $cm.^3/g.$ Powder	Density, $kg./m.^3$ ($lb./ft.^3$)		Density Ratio, Cast:Fired	Water Balance, wt.-% on Fired Sample				
		As Cast	After Firing*		As Cast	Loss on Drying	Loss on Firing	Total Loss	Excess
Thermo-Sil 120	0.12	1911 (119.3)	1788 (111.6)	0.935	12.0	6.9	4.6	11.5	0.5
	0.13	1897 (118.4)	1794 (112.0)	0.946	13.0	7.3	5.1	12.4	0.6
	0.14	1882 (117.5)	1791 (111.8)	0.951	14.0	7.6	5.2	12.8	1.2
	0.15	1842 (115.0)	1769 (110.4)	0.960	15.0	7.8	5.0	12.8	2.2
Fusil S-820	0.13	1850 (115.5)	1735 (108.3)	0.938	13.0	6.0	5.5	11.5	1.5
	0.15	1868 (116.6)	1796 (112.1)	0.961	15.0	7.8	5.9	13.7	1.3
	0.16	1887 (117.8)	1783 (111.3)	0.945	16.0	8.2	6.9	15.1	0.9
	0.17	1887 (117.8)	1765 (110.2)	0.935	17.0	7.8	7.8	15.6	1.4
Resco RS-17E	0.12	2217 (138.4)	2105 (131.4)	0.949	12.0	5.2	5.5	10.7	0.3
	0.13	2139 (133.5)	2055 (128.4)	0.962	13.0	1.2	11.3	11.5	1.5
	0.14	2089 (130.4)	1994 (124.5)	0.955	14.0	6.7	5.6	12.3	1.7
Resco AA-22	0.063	2722 (169.9)	2658 (165.9)	0.976	5.9	6.3	3.4	9.7	-3.8
	0.068	2797 (174.6)	2687 (167.7)	0.960	6.4	6.6	3.5	10.1	-3.7
	0.073	2821 (176.1)	2664 (166.3)	0.944	6.8	6.0	4.4	10.4	-3.6
	0.10	2544 (158.8)	2473 (154.4)	0.972	9.1	9.6	4.4	14.0	-4.9

TABLE 6. PERMEABILITY OF CAST REFRACTORIES

Castable	Casting Water, $cm.^3/g.$ powder	Permeability, centidarcy		Permeability Ratio Fired: Cast
		As Cast	After Firing*	
Thermo-Sil 120	0.12	0.063	0.131	2.08
	0.13	0.074, 0.188	0.125, 0.854	1.69, 4.54
	0.14	0.149	0.225	1.51
	0.15	0.151, 0.157	0.465, 0.501	3.08, 3.19
Fusil S-820	0.13	0.095, 0.095	0.220, 0.220	2.32, 2.32
	0.15	0.083, 0.082	0.134, 0.259	1.63, 3.16
	0.16	0.100	0.138	1.38
	0.17	0.088, 0.087	0.170, 0.230	1.93, 2.64
Resco RS-17E	0.12	0.063	0.153, 0.144	2.43
	0.13	0.138	0.247	1.79
	0.14	0.127	0.413	3.25
	0.15	–	0.408	–
	0.16	–	0.564	–
Resco AA-22	0.063	0.187	0.380	2.03
	0.068	0.190	0.428	2.25
	0.073		0.659	
	0.10	0.339	2.16	6.37

* AT 704°C (1300 °F) FOR 1.5 HOUR

TABLE 7. MODULUS OF RUPTURE OF CAST REFRACTORIES

Material	Casting Water, $cm.^3/g.powder$	Modulus of Rupture, MPa (psi) As Cast	Modulus of Rupture, MPa (psi) After Firing*	Modulus Ratio, Fired:Cast
Thermo-Sil 120	0.12	6.60(957)	4.81(688)	0.72
	0.13	6.38(926)	4.99(714)	0.77
	0.14	7.34(1064)	4.44(636)	0.60
	0.15	6.47(939)	4.40(630)	0.67
Fusil S-820	0.13		6.53(948)	0.70
	0.15 7.83	9.28(1346) (1136)	5.66(821)	0.72
	0.16 7.29	7.98 (1058)	5.44(783)	0.74
	0.17 6.12	5.62 (887)	4.05(587)	0.60
Resco RS-17E	0.12	19.6(1982)	10.2(1455)	0.73
	0.13	8.58(1244)	6.82(977)	0.79
	0.14	9.54(1384)	6.45(923)	0.67
	0.15	9.18(1332)	6.34(908)	0.68
Resco AA-22	0.063	13.6(1976)	11.3(1624)	0.82
	0.068	16.4(2383)	12.6(1809)	0.76
	0.073	12.0(1738)	11.2(1599)	0.92
	0.10	6.22(902)	4.78(694)	0.77

*At 704°C (1300°F)/1.5 hr.

TABLE 8. COMPRESSIVE STRENGTH OF CAST REFRACTORIES

Material	Firing Temperature °C (°F)*	Casting Water, $cm.^3/g.powder$	Compressive Strength MPa (psi)	Number of Replicates
Thermo-Sil	704 (1300)	0.14	18.7(2713)	3
120	704 (1300)	0.15	18.2(2635)	2
	1093(2000)	0.14	17.9(2600)	4
	1093(2000)	0.15	17.4(2532)	3
Fusil S-820	704 (1300)	0.15	23.2(3367)	3
	704 (1300)	0.16	22.4(3253)	3
	1093(2000)	0.15	24.1(3495)	4
	1093(2000)	0.16	20.5(2977)	3
	1371(2500)	0.13	35.5(5142)	6
	1371(2500)	0.15	21.5(3125)	6
	1371(2500)	0.16	27.8(4033)	3
	1371(2500)	0.17	20.9(3033)	6
Resco RS-17E	704 (1300)	0.13	19.3(2800)	1
	704 (1300)	0.14	19.4(2810)	1
	1093(2000)	0.13	18.1(2630)	2
	1093(2000)	0.14	15.9(2300)	1
	1371(2500)	0.15	18.3(2661)	9
Resco AA-22	704 (1300)	0.073	32.6(4733)	3
	704 (1300)	0.10	14.5(2117)	3
	1093(2000)	0.073	36.1(5243)	3
	1093(2000)	0.10	17.9(2593)	3
	1371(2500)	0.073	52.1(7555)	6
	1371(2500)	0.10	12.5(1810)	6

*Time of firing was 1.5 hr.

TABLE 9. COEFFICIENT OF LINEAR THERMAL EXPANSION OF CAST REFRACTORIES

Material *	Casting Water, cc/g.	Coefficient of Linear Thermal Expansion, 10^{-6} cm./cm/^{o}C (10^{-6} in./in./^{o}F	Temperature Range, ^{o}C, Over Which Coefficient is Averaged	Wt. Loss, %, During Test
Thermo-Sil 120	0.14	1.2 (0.7)	24-704	0.57
Fusil S-820	0.15	1.0 (0.6)	535-704	3.3
Resco RS-17E	0.12	6.7 (3.7)	24 704	1.1
Resco AA-22	0.068	7.8 (4.3)	24-704	0.079

* Fired at 704^{o}C (1300^{o}F)/1.5 hr.

NOTE: Samples were dried at 315^{o}C (599^{o}CF)/16 hr. to remove water not reacted during cure and/or introduced by water-cooled cutting.

TABLE 10. Physical Properties of Porous Tools and C-Scan Results on 12-Ply Laminates of PMR-15

Material *	Casting Water, $cm.^3/g.$ powder	Modulus of Rupture MPa (psi)	Permeability, Centidarcy	C-Scan Results on PMR-15 Laminate	Tool Surface
Thermo-Sil 120	.12	4.74 (688)	.131	Total Defect	Smooth
Thermo-Sil 120	.13	4.92 (714)	.125	3 Spots Defect	Smooth
Thermo-Sil 120	.14	4.39 (636)	.225	2 Spots Defect	Rough
Thermo-Sil 120	.15	4.34 (630)	.465	1 Spot Defect	Rough
Fusil S-820	.13	-	.220	3 Spots Defect	Smooth
Fusil S-820	.14	-	-	Total Defects	Smooth
Fusil S-820	.15	-	.134	3 Spots Defect	Smooth
Resco 17-E	.12	10.0 (1450)	.153	2 Spots Defect	Smooth
Resco 17-E	.13	7.74 (1128)	.247	Acceptable	Smooth
Resco 17-E	.14	6.52 (945)	.413	Good	Smooth
Resco 17-E	.15	6.26 (908)	-	Good	Smooth
Resco AA-22	.063	10.0 (1457)	.380	3 Spots Defect	Rough
Resco AA-22	.068	12.5 (1811)	.428	Defects	Very Rough
Resco AA-22	.073	11.3 (1637)	-	Defects	Rough
Resco AA-22	.100	6.89 (1000)	2.16	Good	Smooth

* Fired at 704°C (1300°F)/2 Hr.

TABLE 11

FIBER VOLUME, PLY THICKNESS AND DENSITY OF LAMINATES BY TWO METHODS

PANEL† NO.	SPECIMEN NO.	FIBER VOLUME		PLY THICKNESS(in.)		DENSITY	
		PHOTO MEAS.	GRAVIMETRIC CALC.*	PHOTO MEAS.	GRAVIMETER CALC.	PHOTO AREA CALC.	GRAVIMETER MEAS.
5A	1	63	62.0	.0055	.0055	1.600	1.600
5B-1	1	63	67.6	.0053	.0052	1.600	1.620
5B-2	1	63	61.1	.0056	.0055	1.600	1.592
9A	2	62	64.4	.0060	.0058	1.596	1.606
9B-1	1	66	64.8	.0048	.0048	1.613	1.608
9B-2	2	62	63.4	.0061	.0060	1.596	1.602
19A	2	60	58.8	.0066	.0064	1.587	1.582
14B-1	2	56	56.9	.0067	.0067	1.570	1.574
14B-2	1	60	58.1	.0047	.0047	1.587	1.579

* P of fiber = 1.760, P of cured resin = 1.328

† A = cured on steel plate

B1 = cured on porous tool with seal on top side

B2 = cured on porous tool with open top side

TABLE 12 PROPERTIES OF 30 x 30 cm. (12 x 12 in.) PMR-15 LAMINATES PREPARED USING RESCO AA-22 POROUS TOOLING

Tool Permeability Centidarcy	Thickness cm. (in.)	Defects, % by C-Scan		Properties of B Panels				
		A* Panel 1	B Panel 2	Flexural Strength, MPa (psi)	Inter-Laminar Shear Strength MPa (psi)	Void Content, Volume-%	Last When Tg °C	°F
--	.070(0.28)	0	0	284.4	-	0.60	353	(667)
0.15	0.15(0.060)	0	0	240.2	16.0	0.26	317	(603)
	0.31(0.120)	52	51	175.6	14.4	0.36	331	(628)
--	0.070(0.028)	0	0	312.4	-	0.56	(352)	(666)
0.25	0.15(0.059	0	1	241.7	14.4	0.54	322	(612)
	0.32(0.124)	-16	-35	187.3	14.7	0.39	355	(671)
--	0.070(0.028)	0	0	301.1	-	0.69	324	(615)
0.35	0.16(0.062	0	0	267.9	16.1	0.86	323	(613)
	0.30(0.119)	0	0	186.6	15.5	0.47	317	(603)
--	0.14(.056)**	0		← (Not Tested) →				
0.35								

*Delivered to NASA - Langley

**(0,+45,90-45), delivered to NASA - Langley

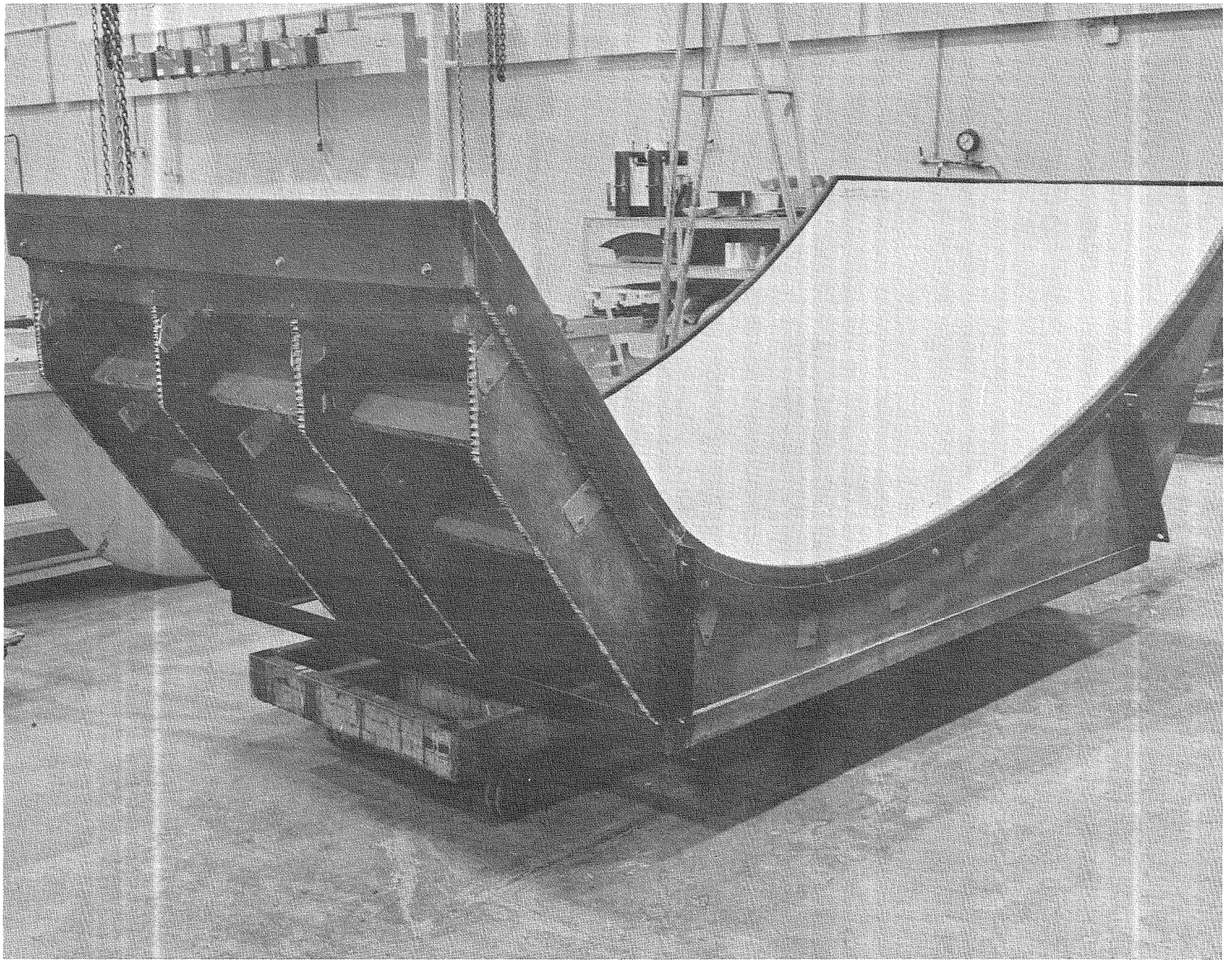


Figure 1. Stainless Steel Fiber Reinforced Ceramic Bond Tool

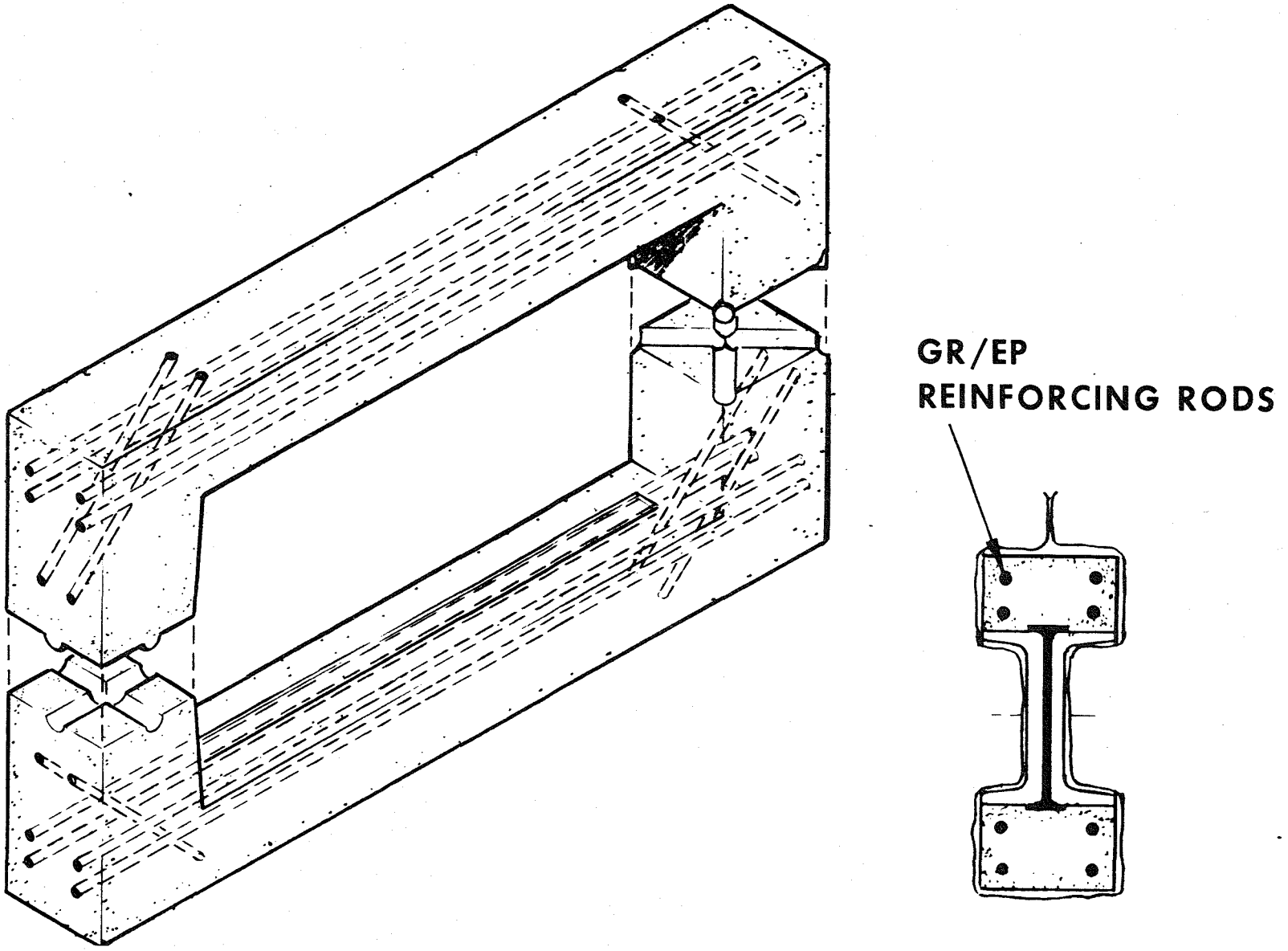


Figure 2 Two-Piece Ceramic Curing Die

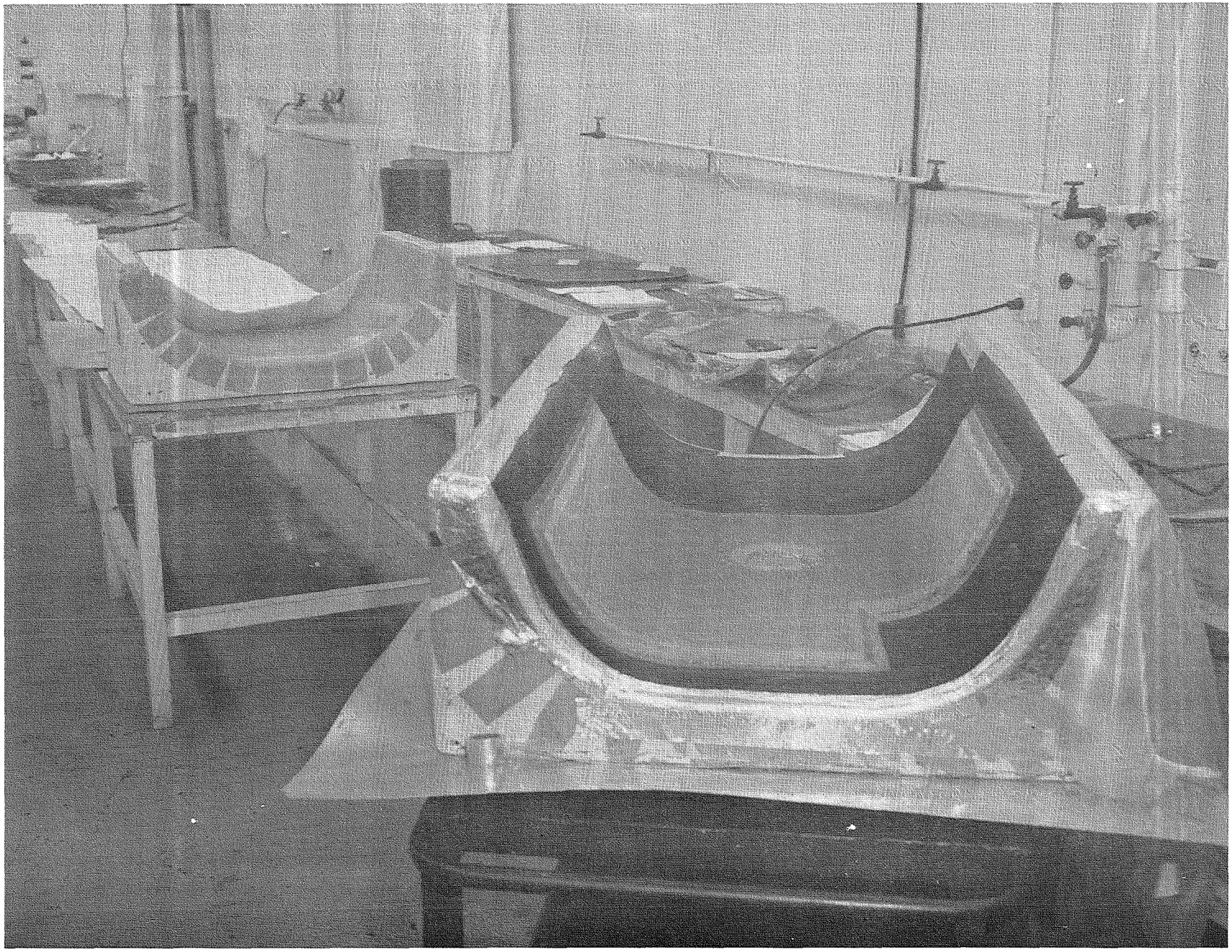


Figure 3. Reinforced Ceramic Lay-up Tool, Fuselage Section, Used for HIMAT Program

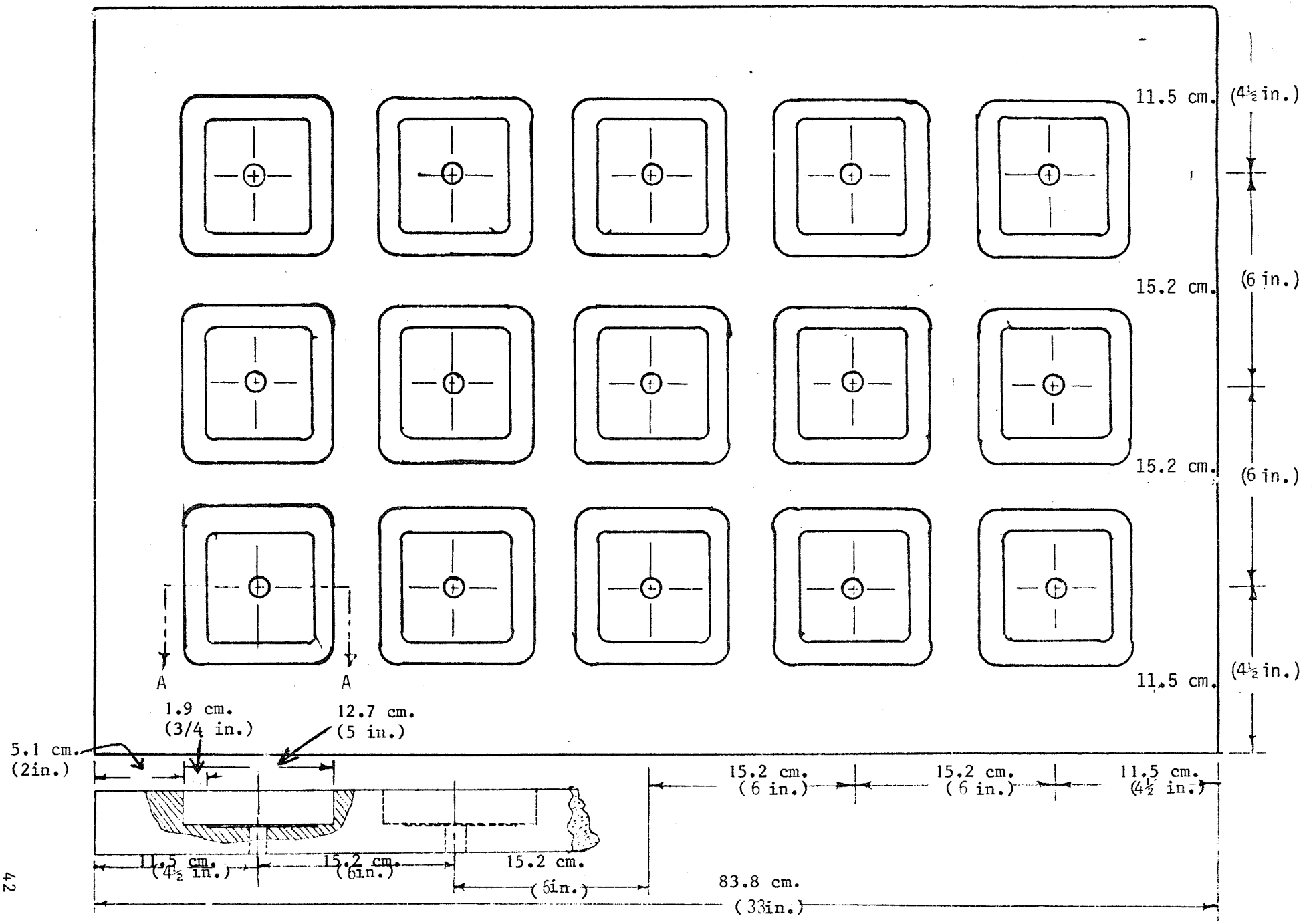


Figure 4. Aluminum Screening Tool Holder

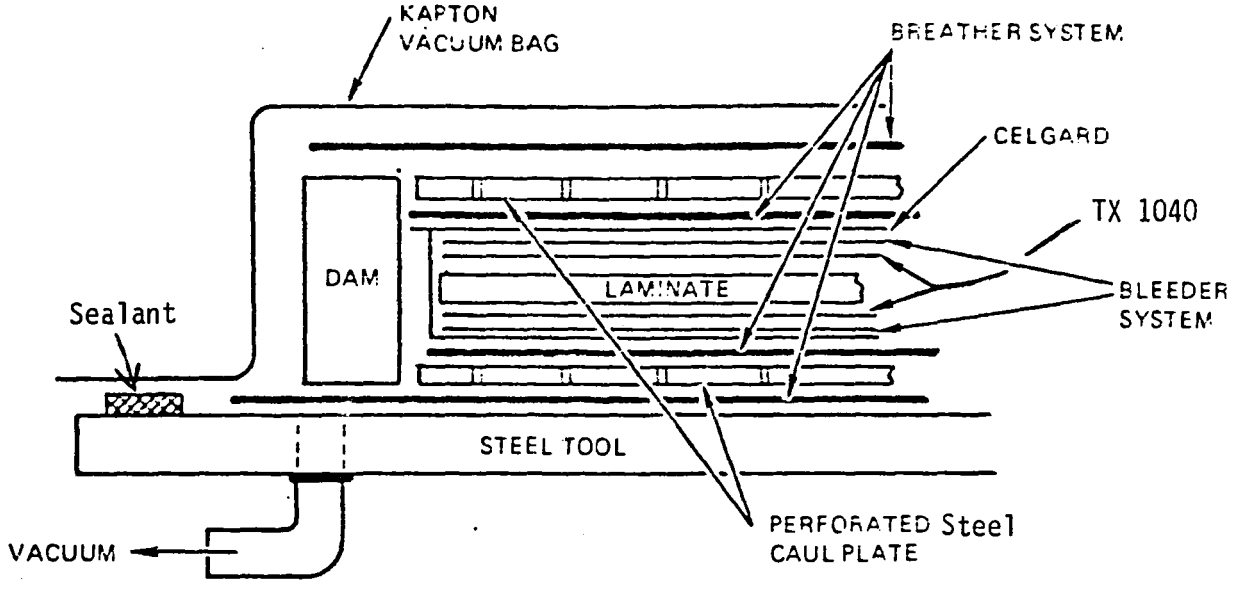


Figure 5

Lay-Up Configuration for Laminates Using Perforated Steel Caul Plates

10 Plies

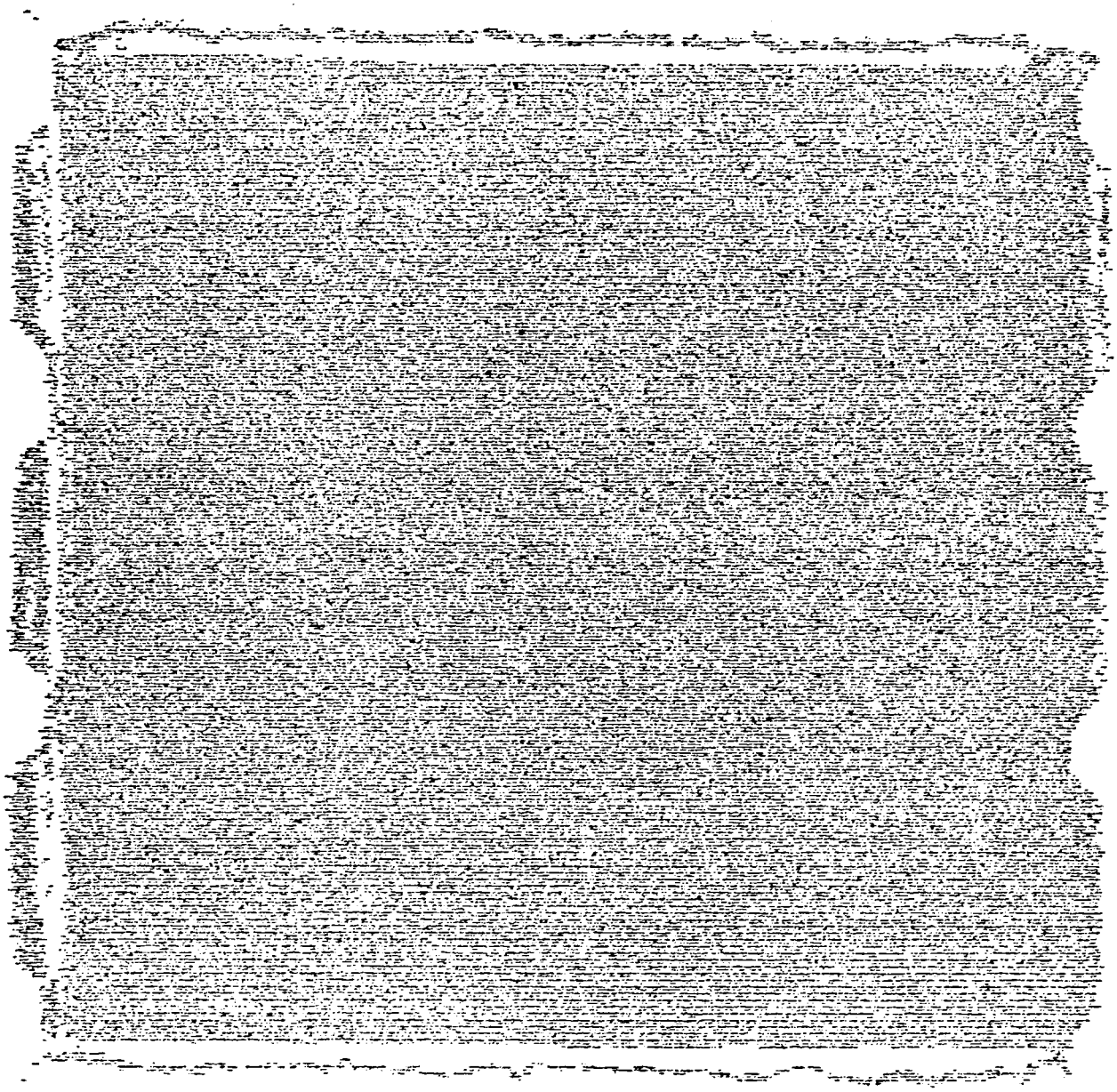


Figure 6

C-Scan on Laminates of 10-13 Plies of PMR-15 Molded Between Perforated Steel Caul Plates (Figure 5)

11 Plies

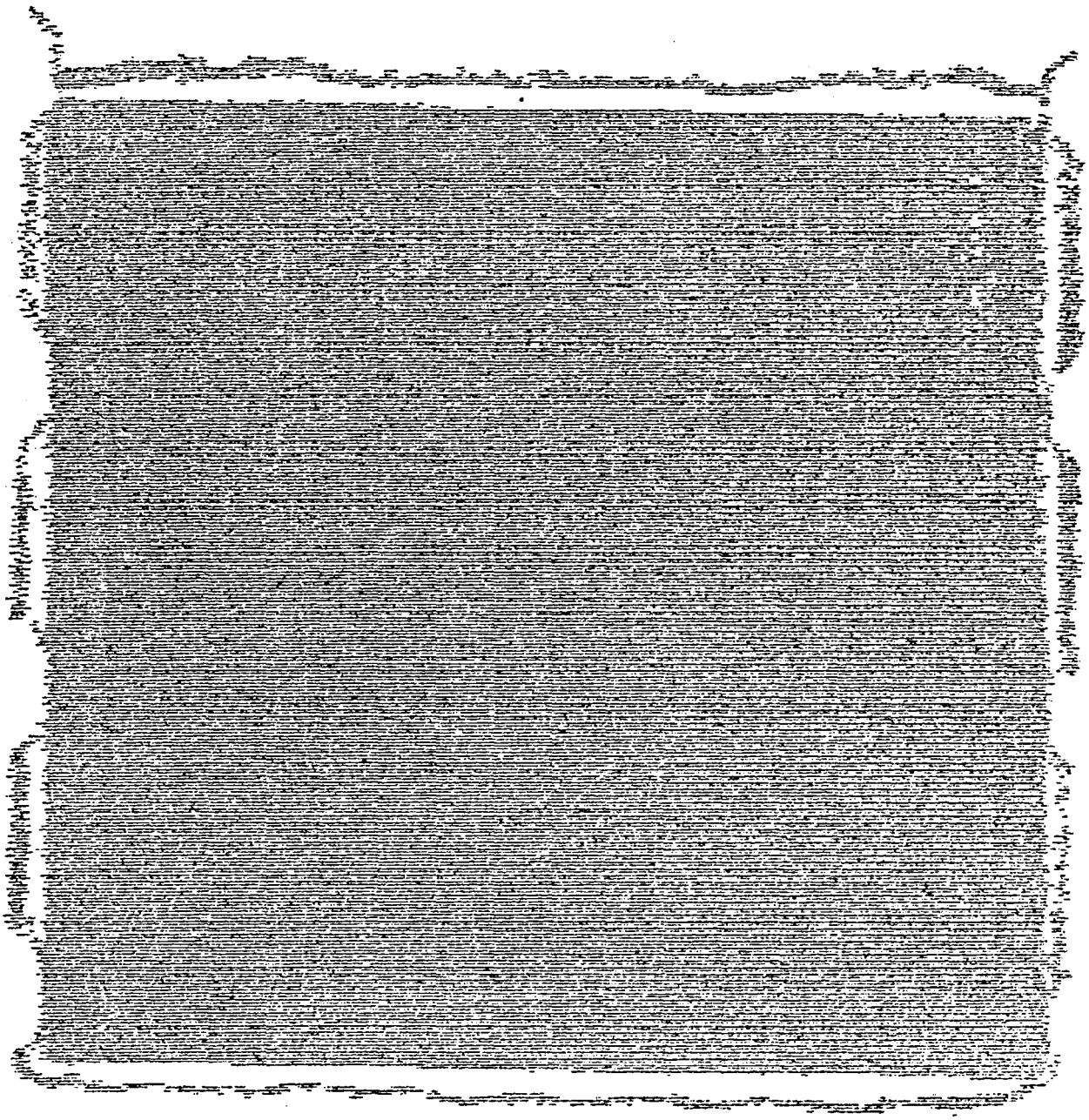


Figure 6 (Continued)

12 Plies

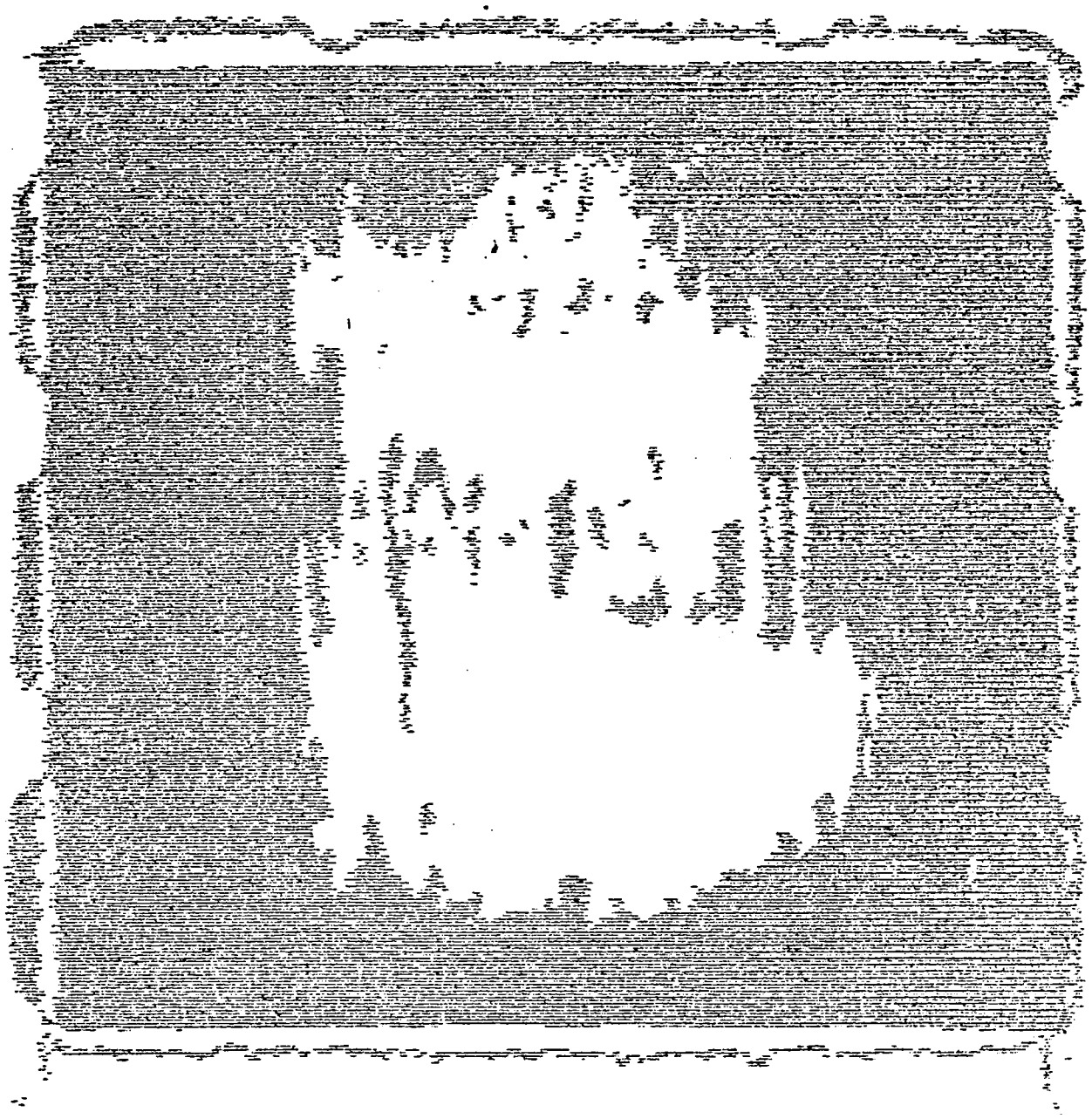


Figure 6 (continued)

13 Plies

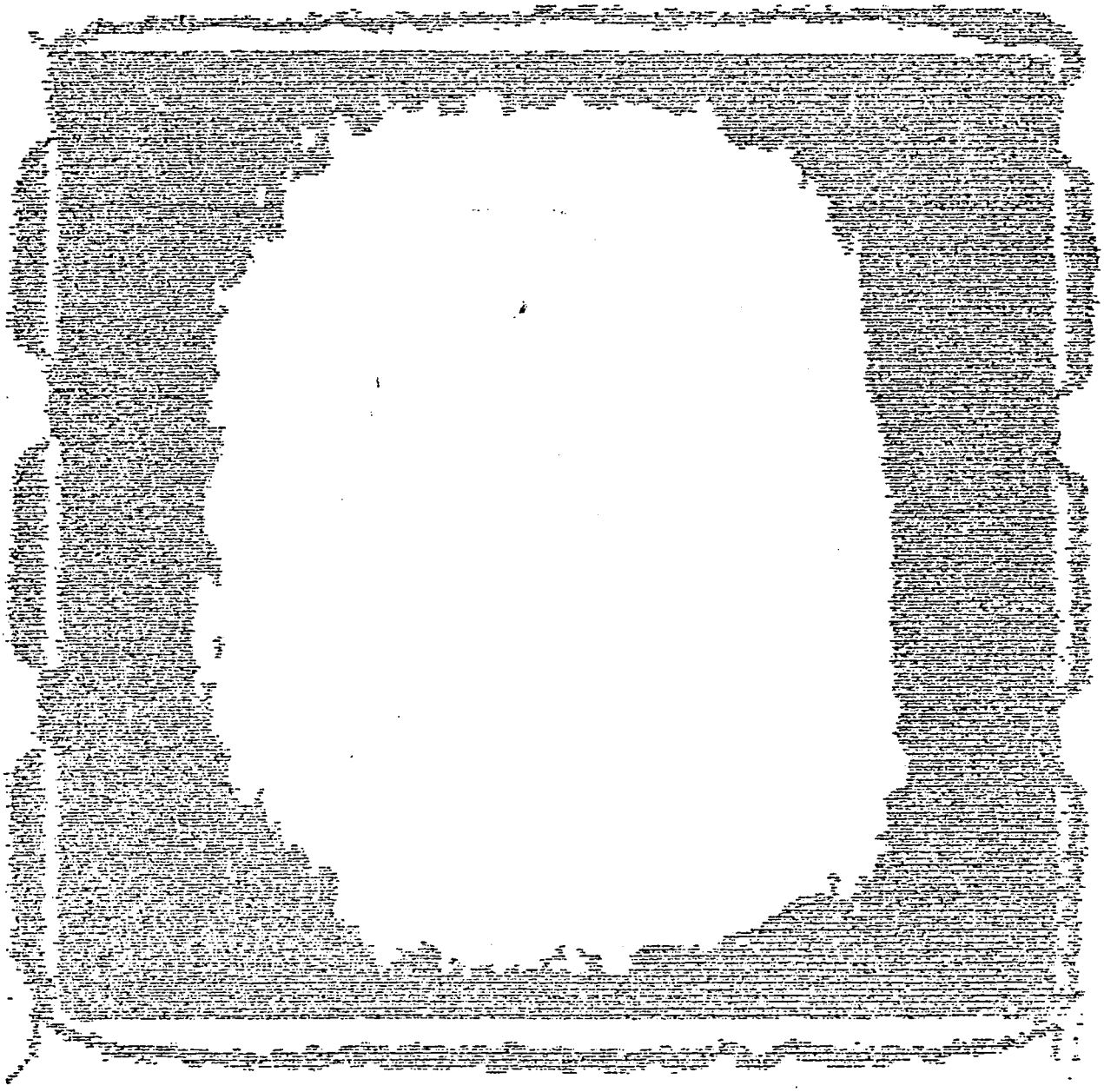


Figure 6 (continued)

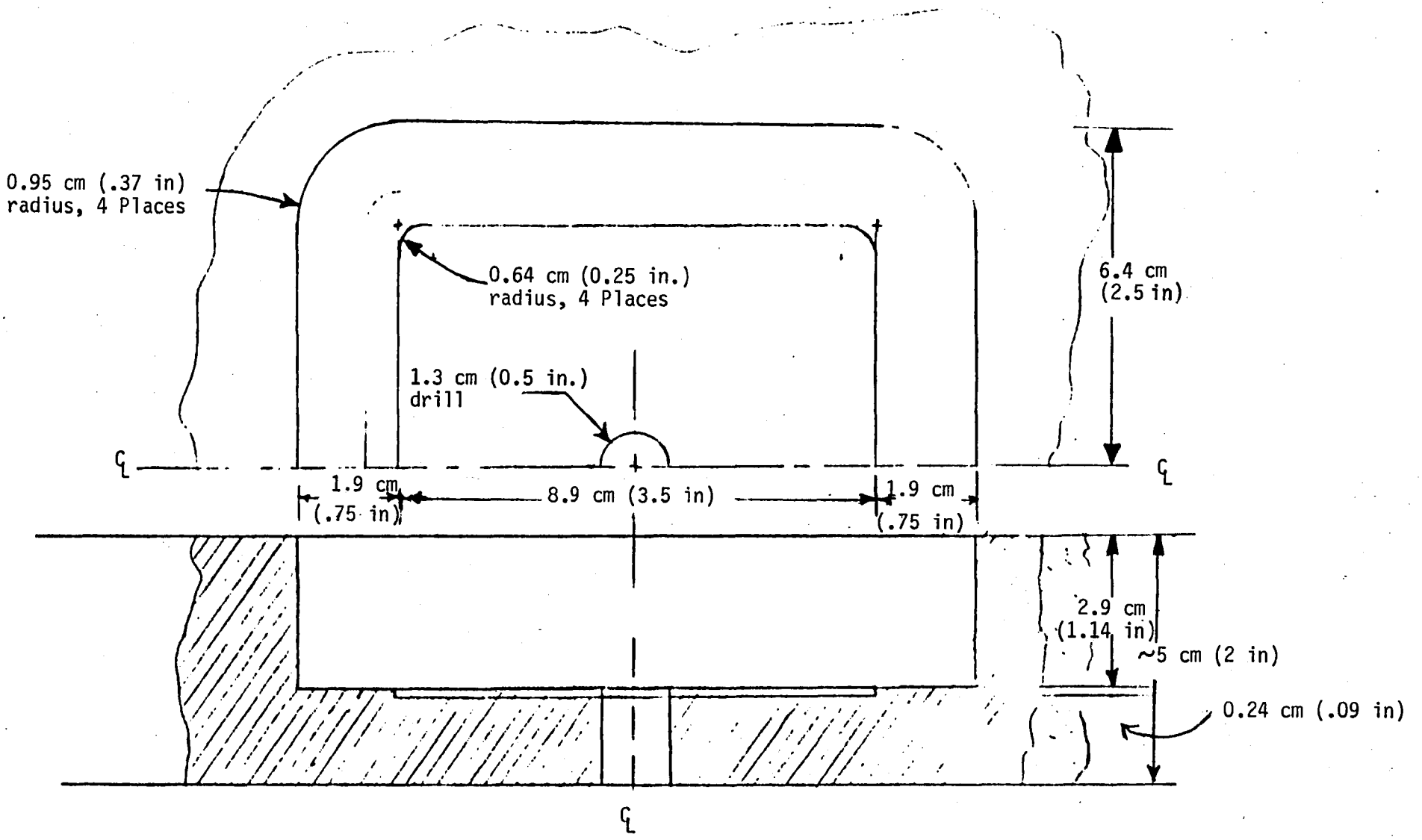


Figure 7. Details of Tool Cavities of Aluminum Holder Used to Contain Ceramic Porous Tools

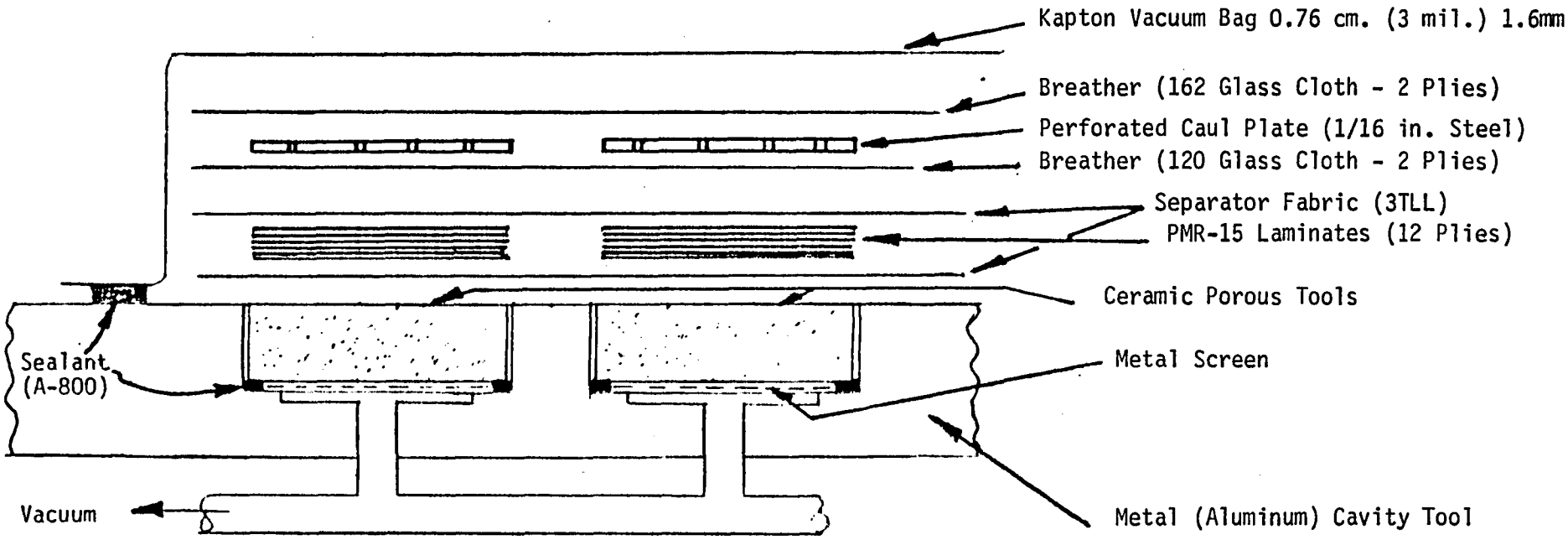


Figure 8. Tooling/Lay-up Configuration for PMR-15 Autoclave Cure Using Porous Ceramic Tools

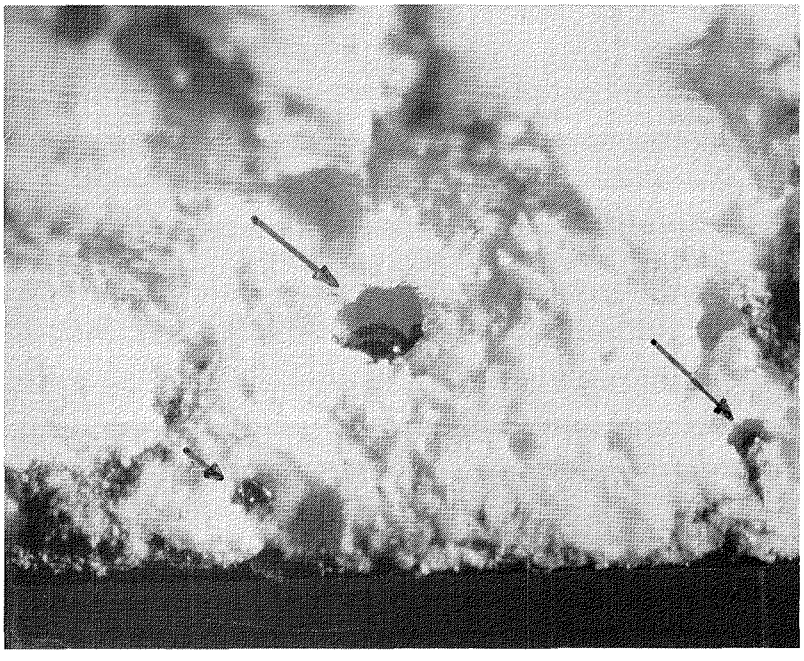


Figure 9. Resin Deposit in Micropores of Ceramic Porous Tools (Approximately 25X)

Figure 10. Three Configurations for Lay-Up of PMR-15 Laminates Using Resco AA-22 Porous Tools

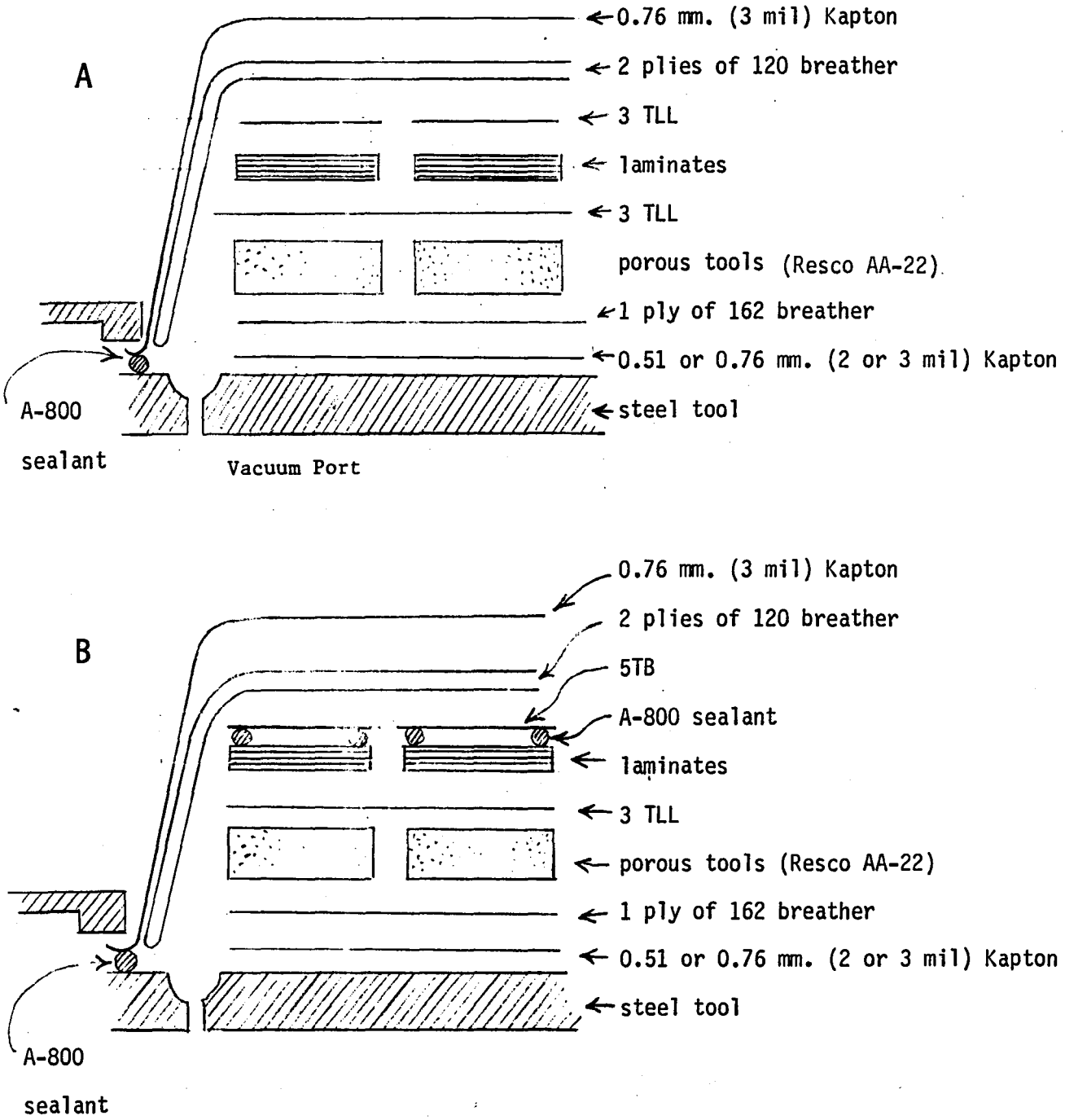
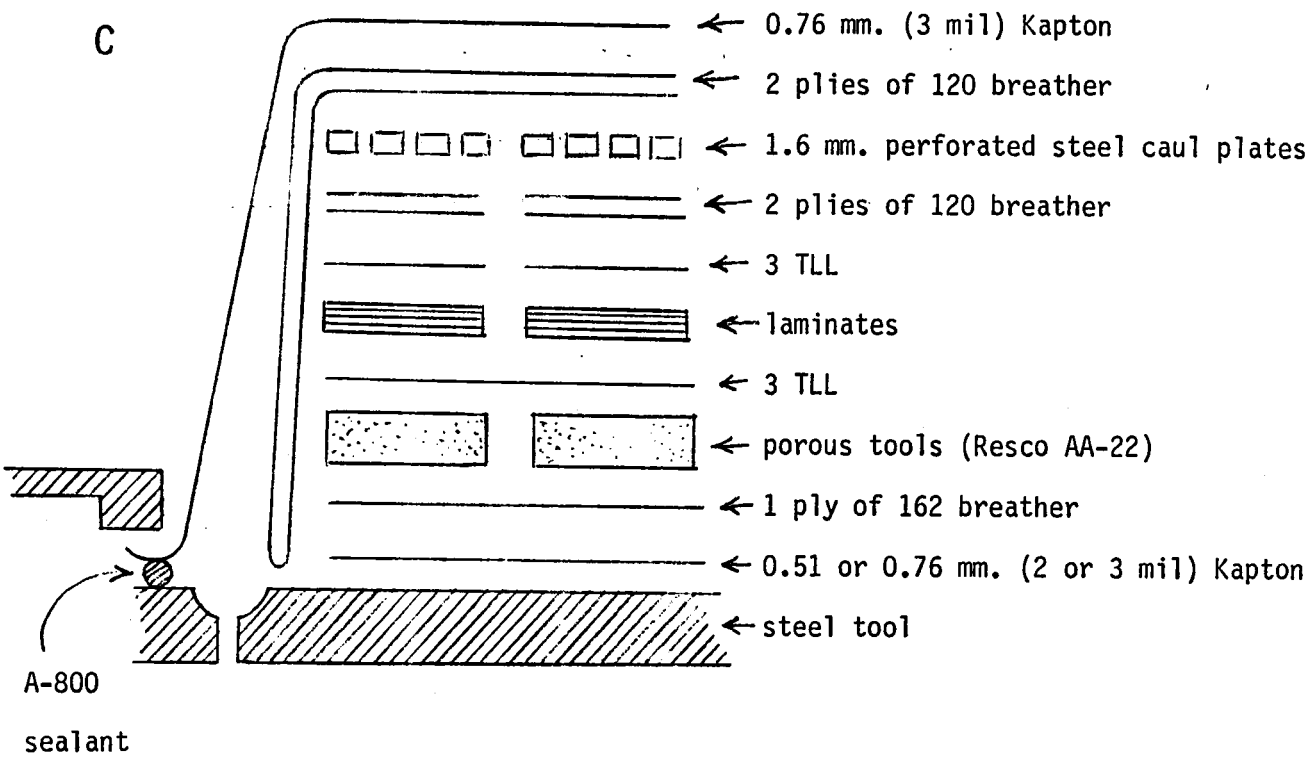


Figure 10. (cont.)



NOTE: The materials are described in Appendix C.2.

Configuration A, 14 Plies

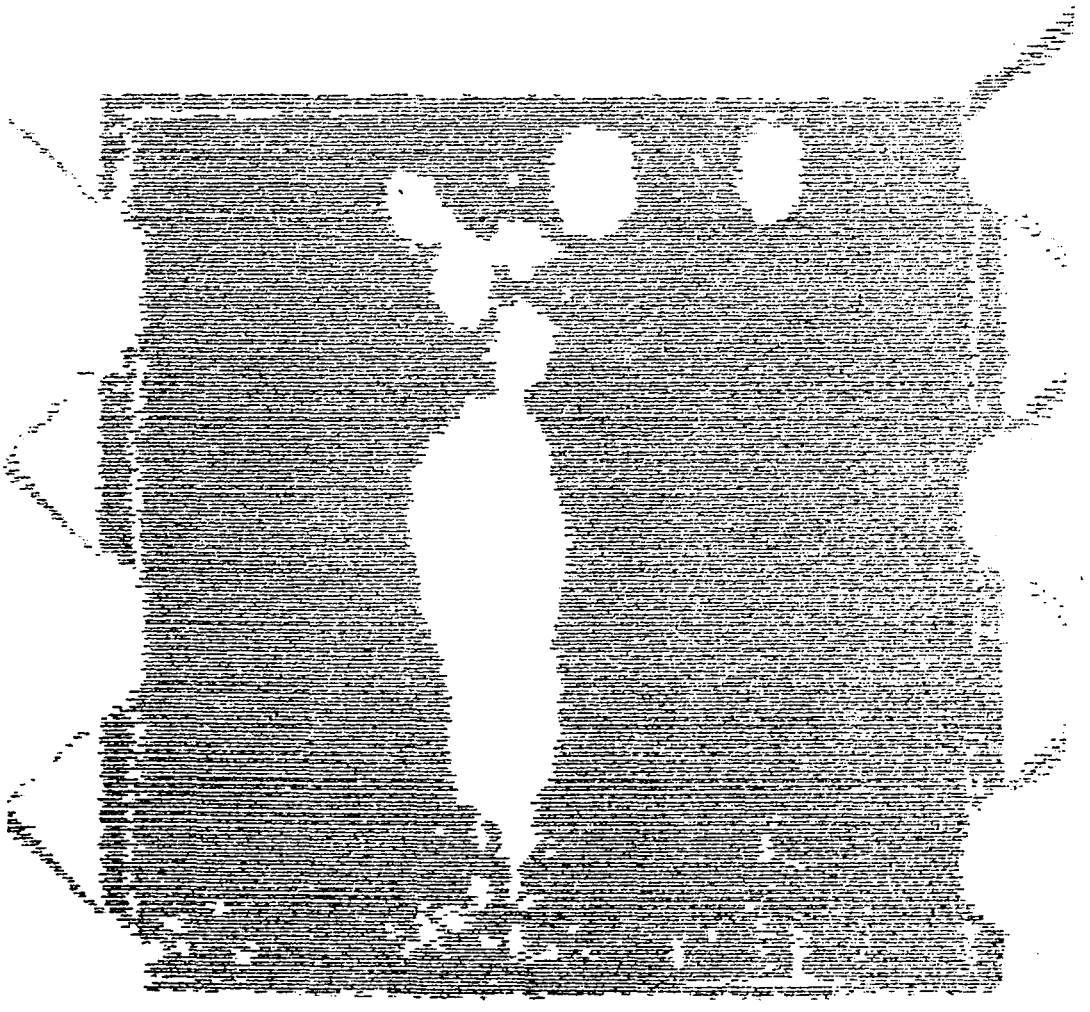


Figure 11

C-Scans of PMR-15 Laminates Using the Three Lay-Up Configuration of Figure 10.

Configuration B, 14 Plies

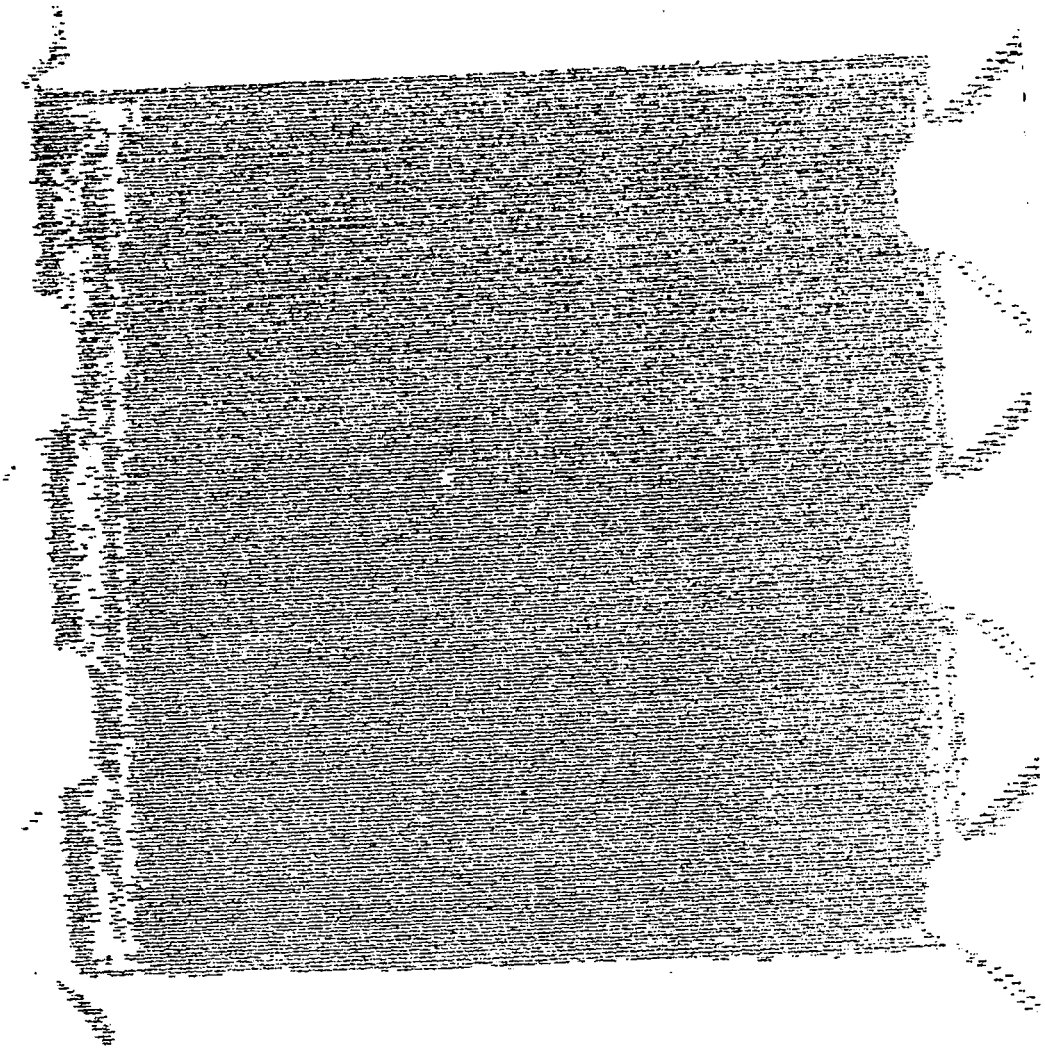


Figure 11 (Continued)

Configuration B, 15 Plies

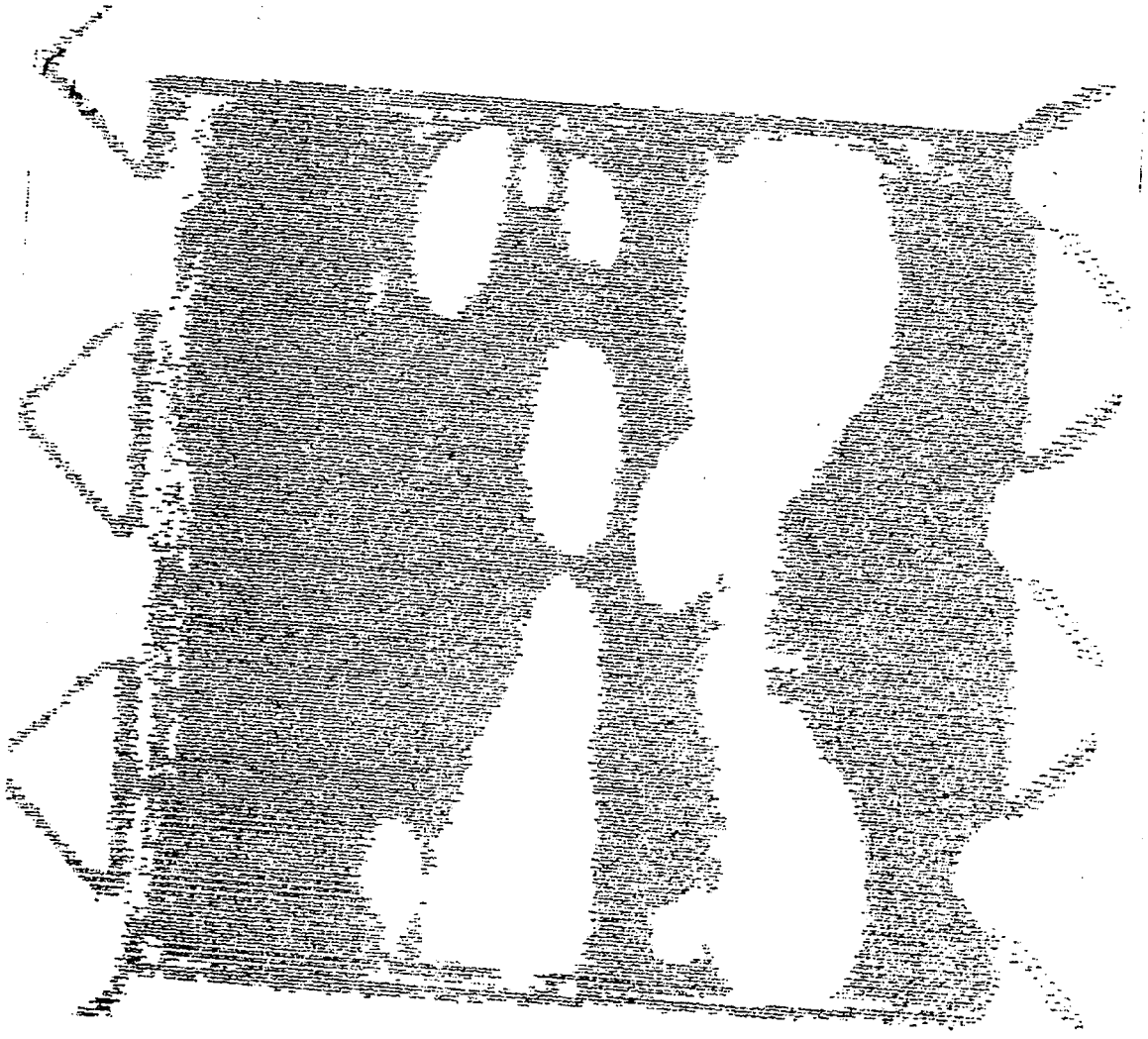


Figure 11 (Continued)

Configuration C, 14 Plies

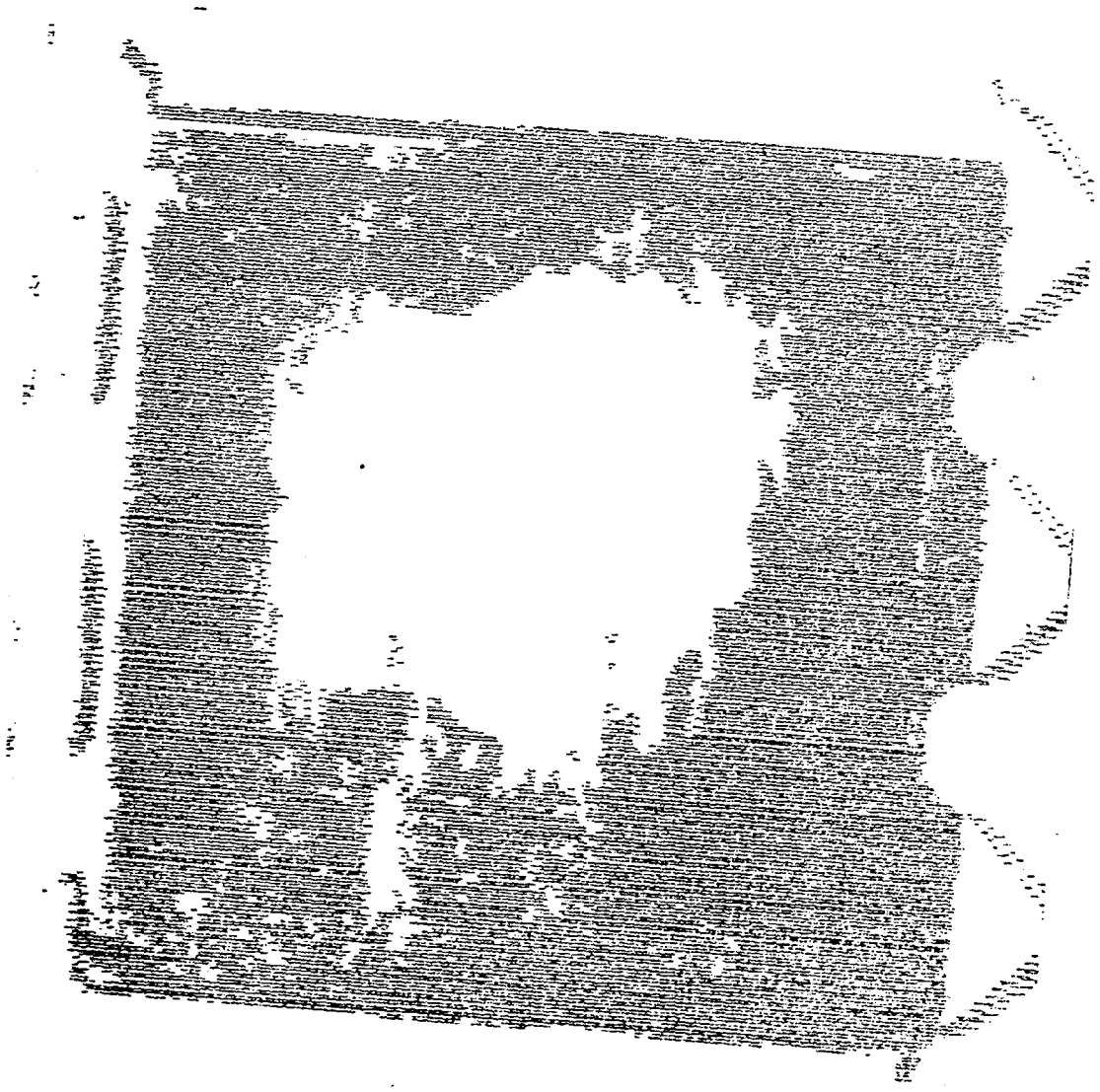
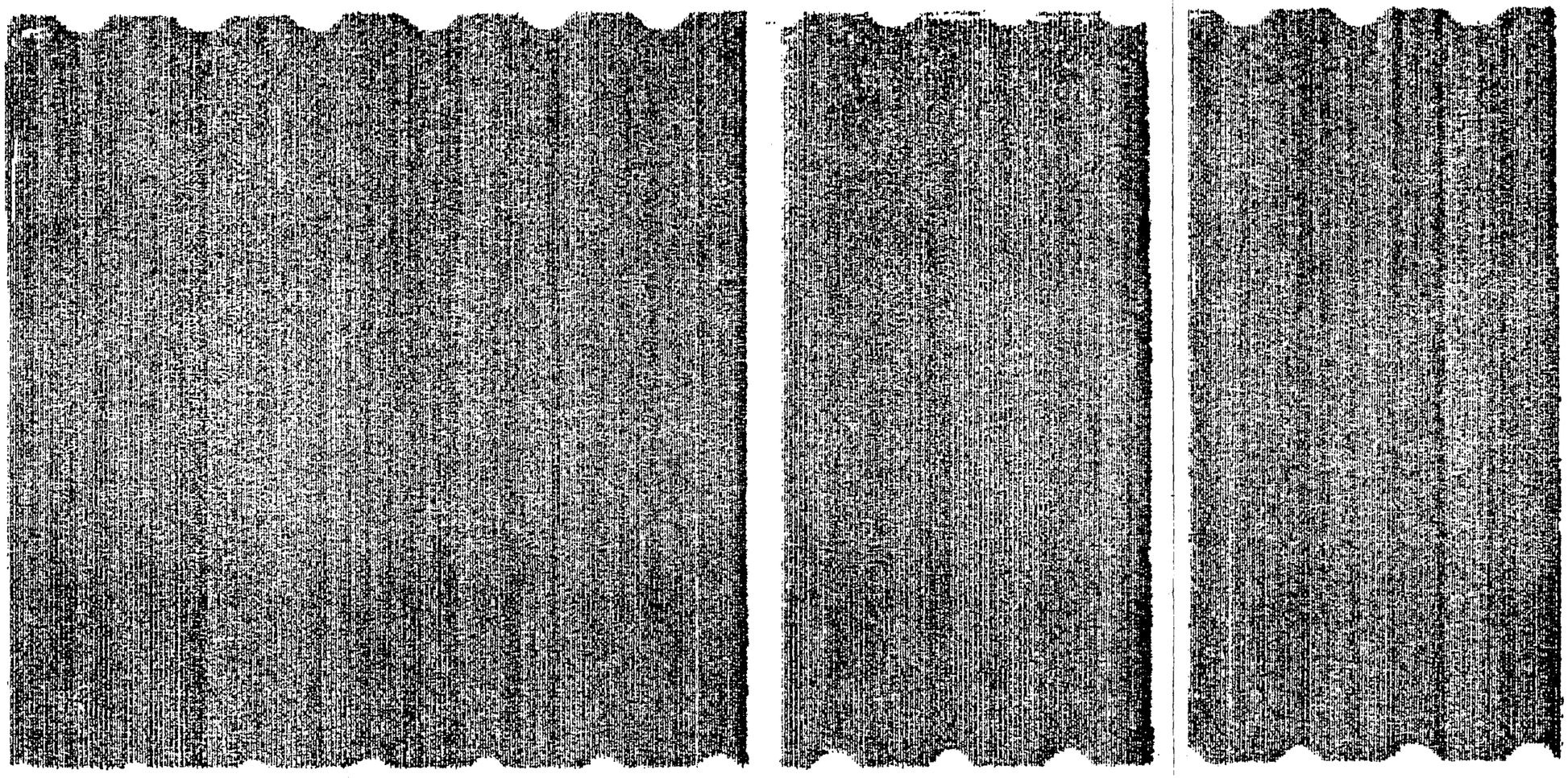
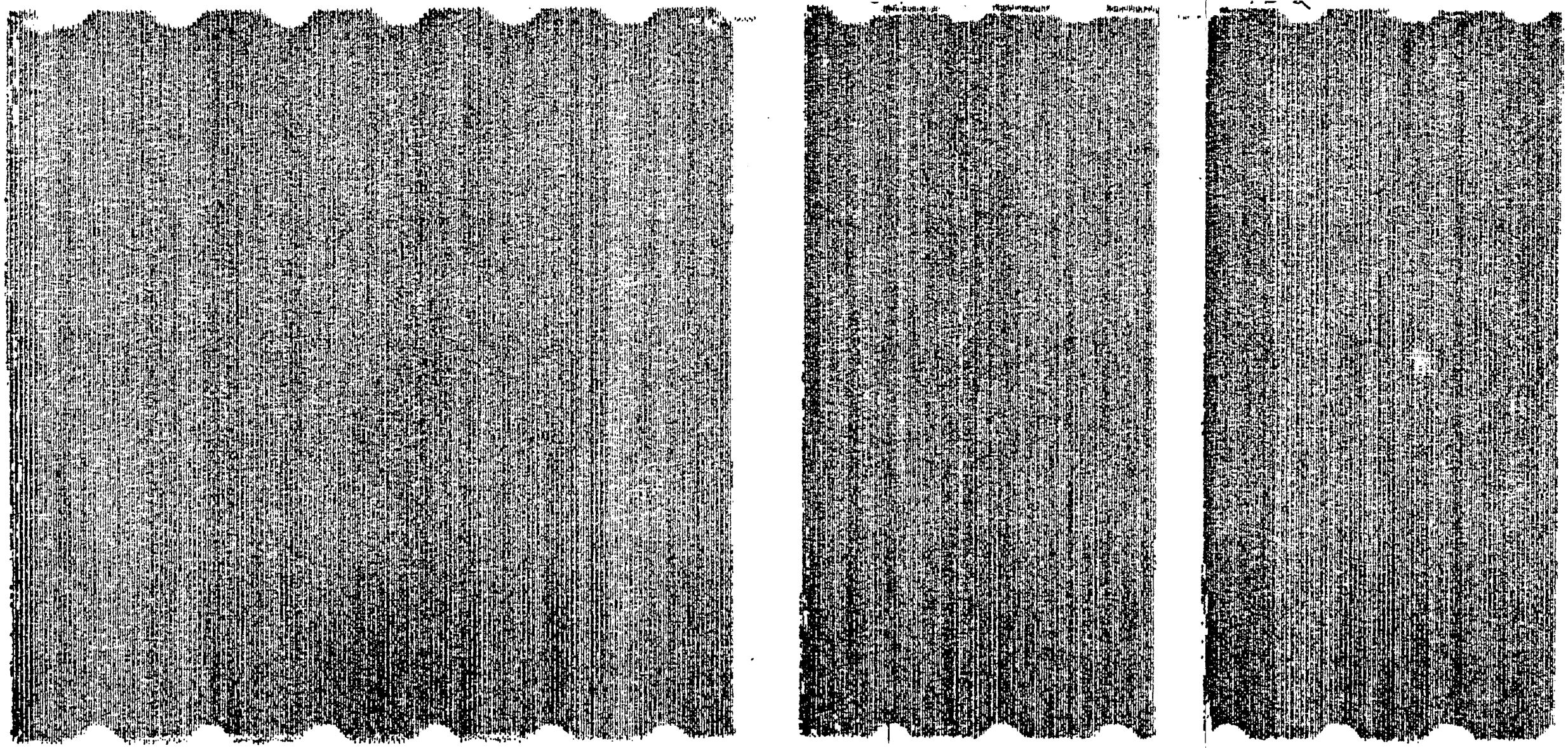


Figure 11 (Continued)



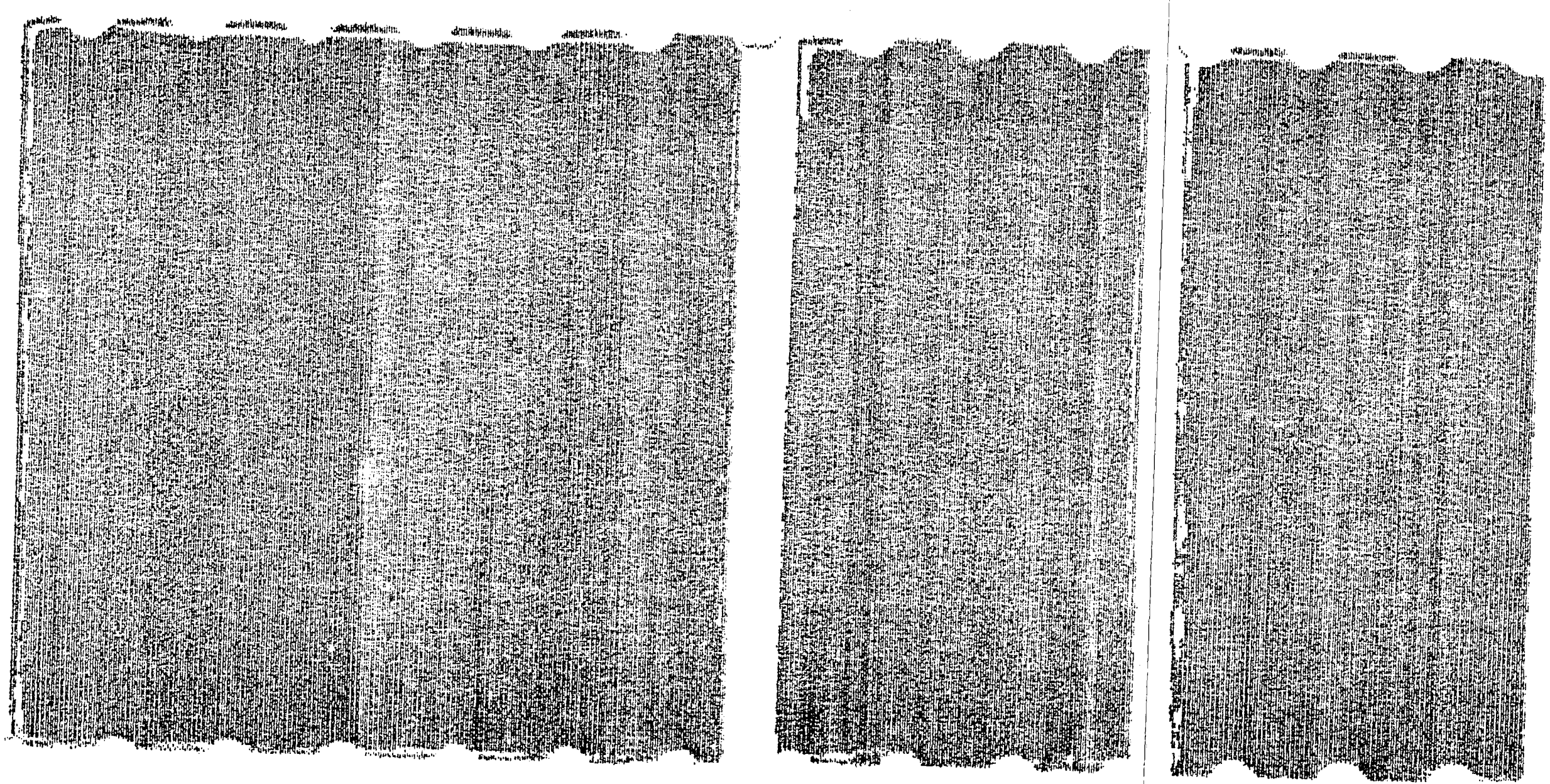
Specimen: 5A 5B-1 5B-2

Figure 12: C-Scan on PMR-15 Laminates of 5, 9, and 14 Plies Produced on Steel "A", on Porous Tool Sealed on Top B1 and Open on Top B2, (See Figure 13)



Speciment: 9A | 9B-1 | 9B-2

Figure 12 (Continued)



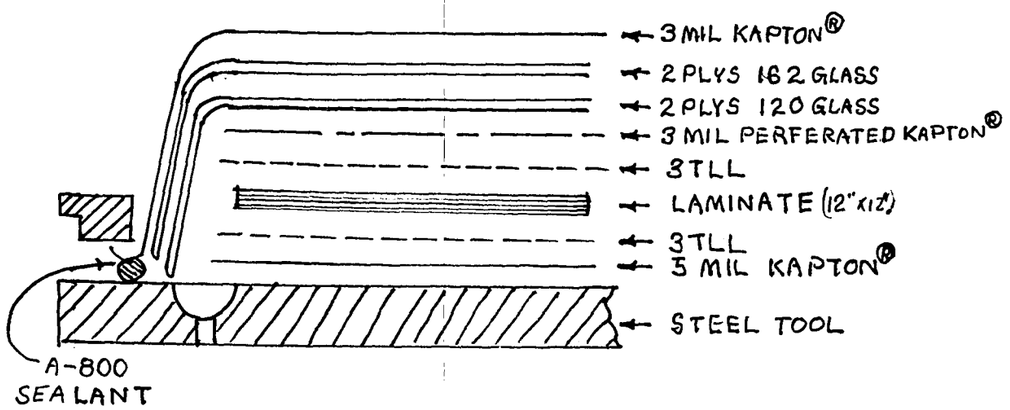
Specimen: 14A

14B-1

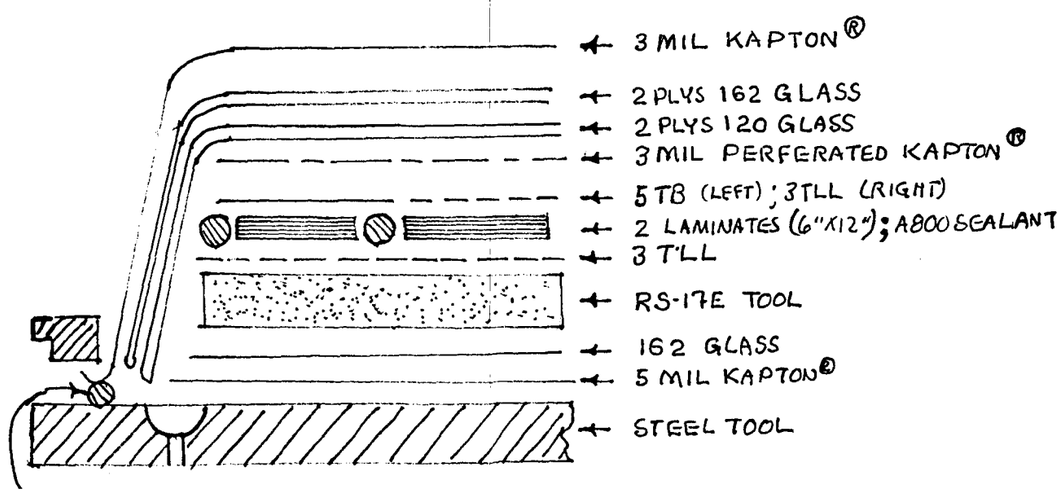
14B-2

Figure 12 (Continued)

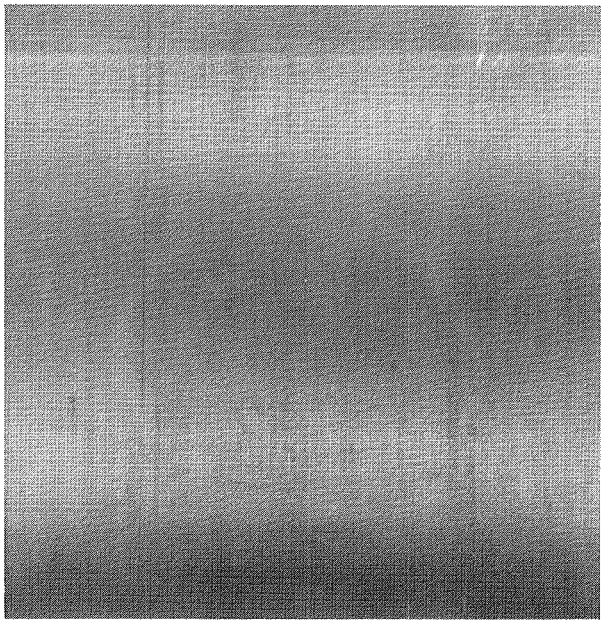
Figure 13. Cure Configurations for RS-17E Tool Check



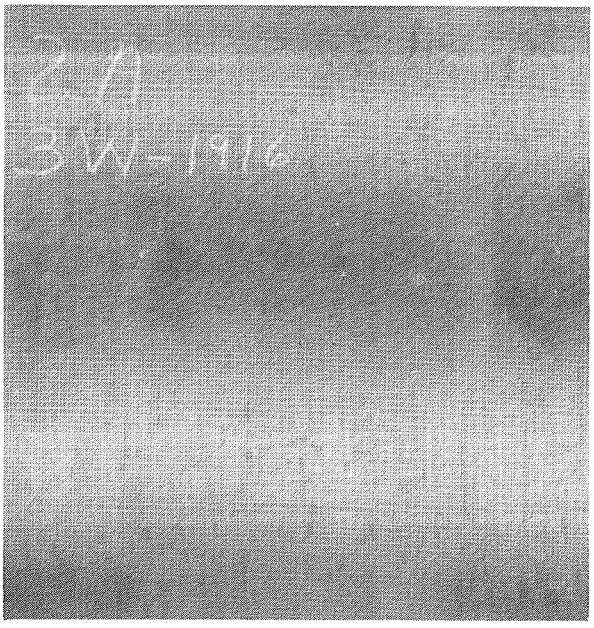
Configuration A



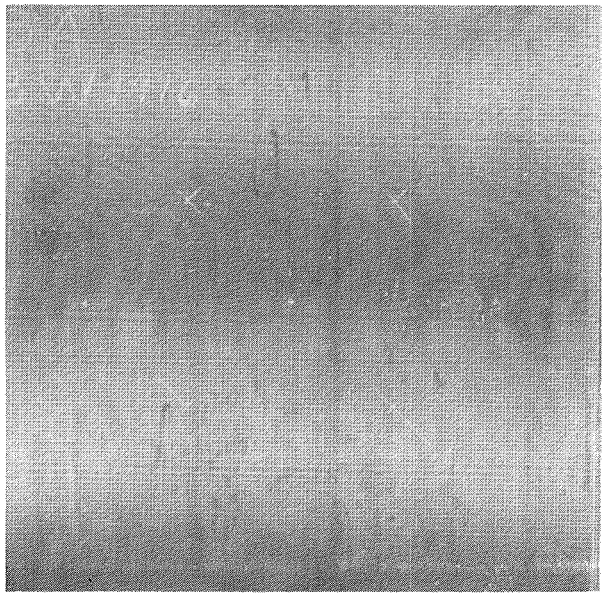
Configuration B-1 (Left) B-2 (Right)



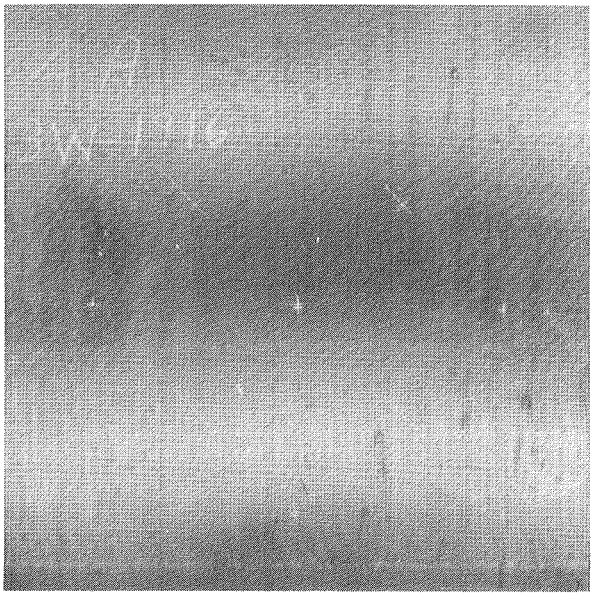
Panel 1A



Panel 2A



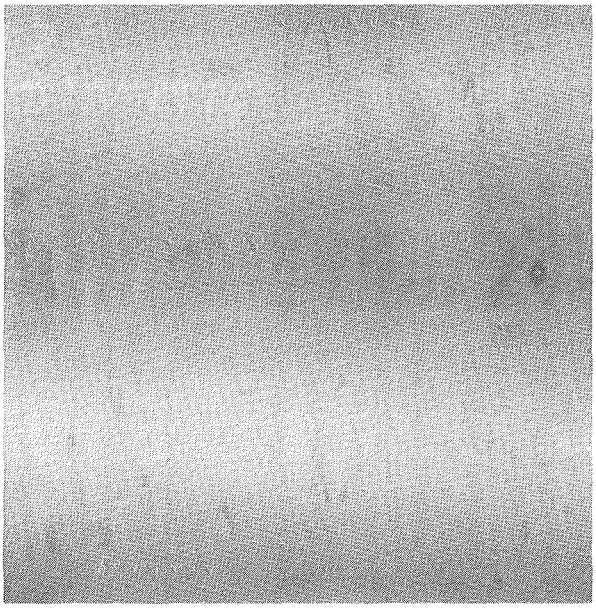
Panel 3A



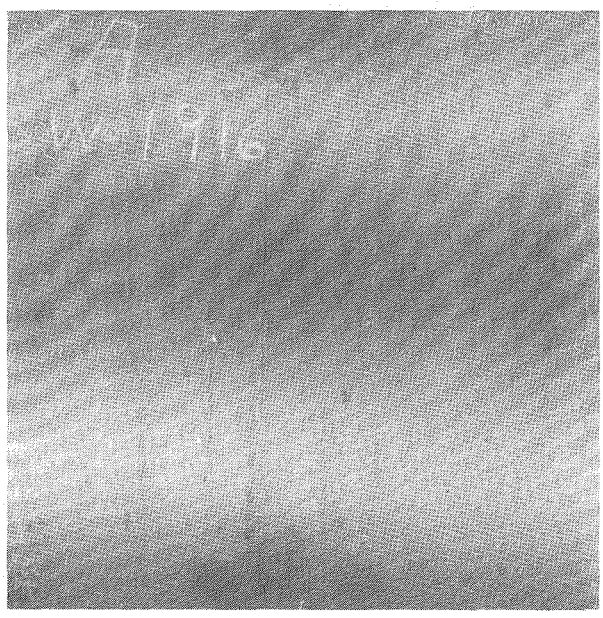
Panel 4A

Figure 14

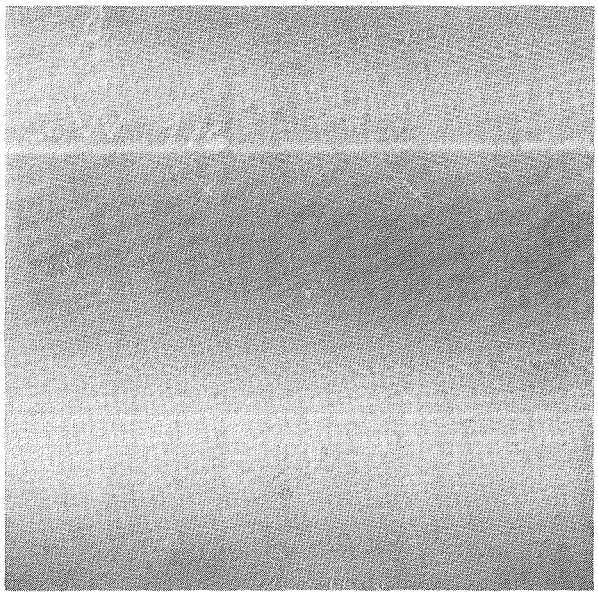
Photograph of 30x30 cm. (12x12 in.) PMR-15 Laminates
Prepared Using Resco 17E Porous Tooling



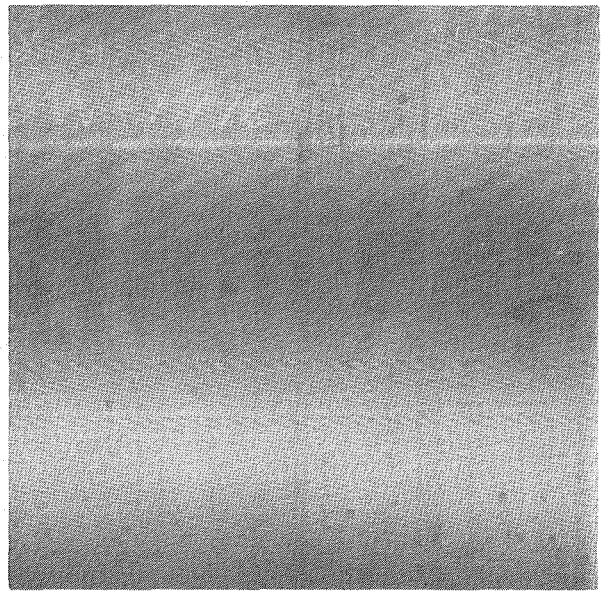
Panel 5A



Panel 6A

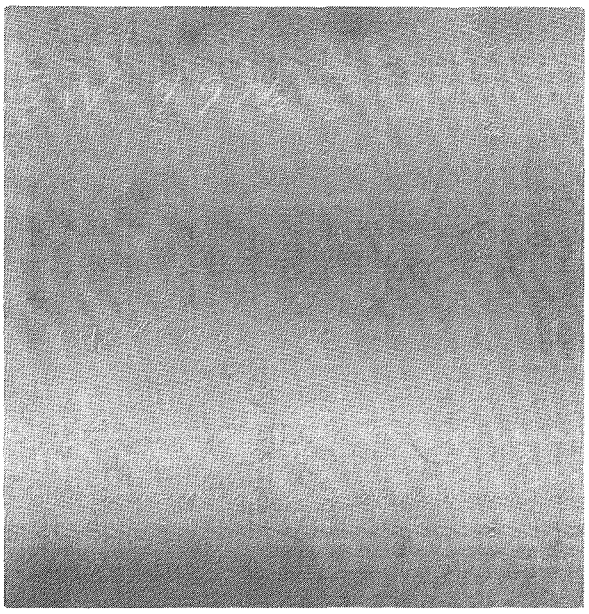


Panel 7A



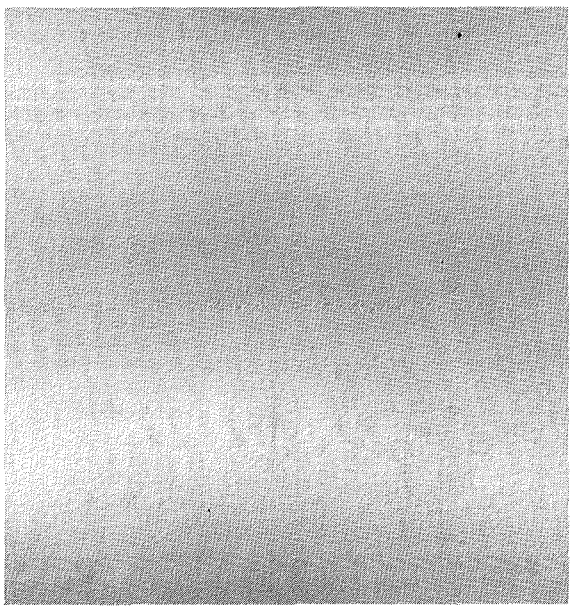
Panel 8A

Figure 14 (Continued)

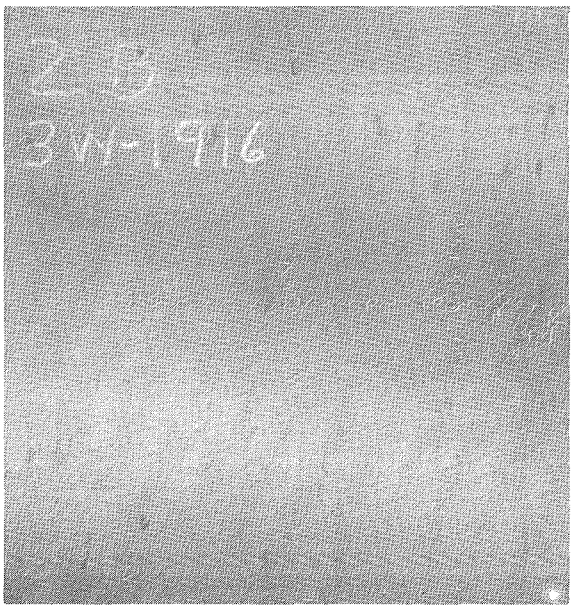


Panel 9A

Figure 14 (Continued)



Panel 1B

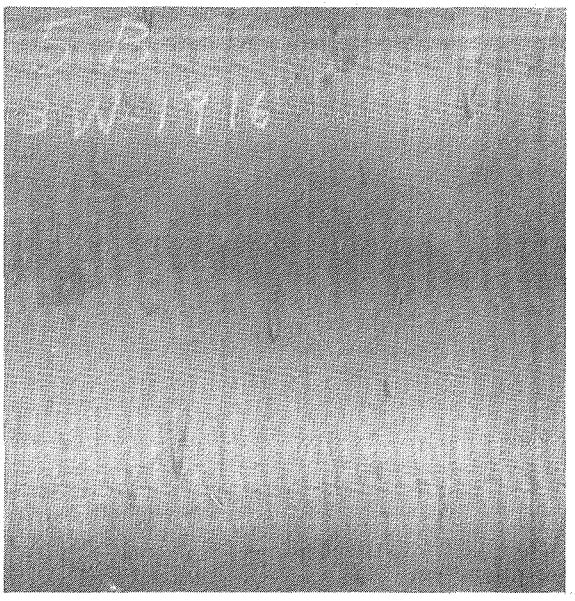


Panel 2B

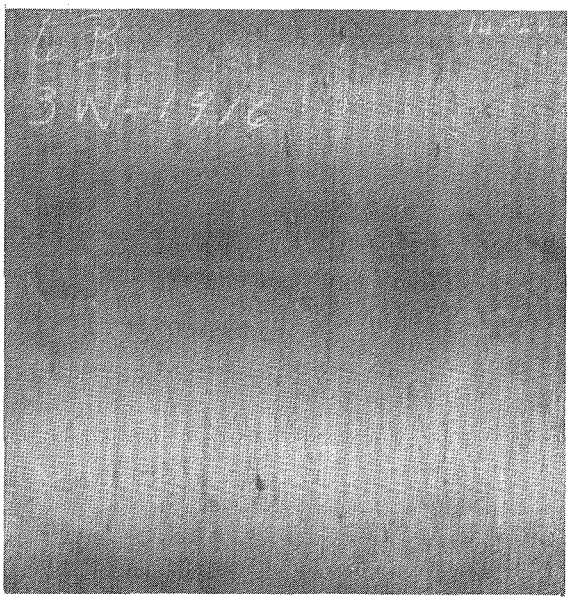
Panel 3B

Panel 4B

Figure 14 (Continued)

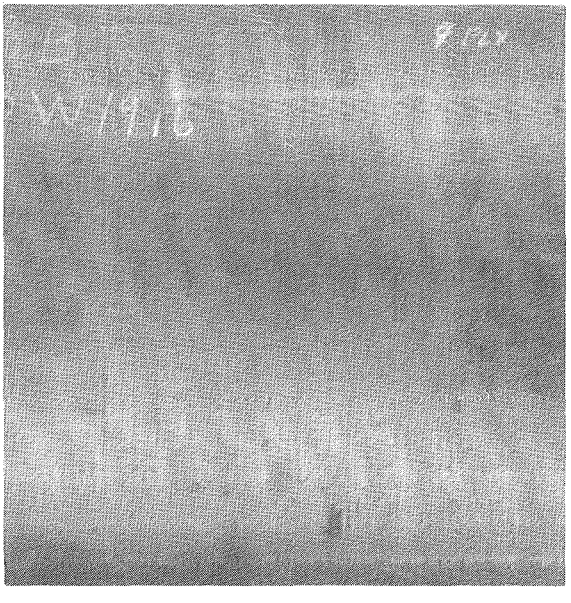


Panel 5B



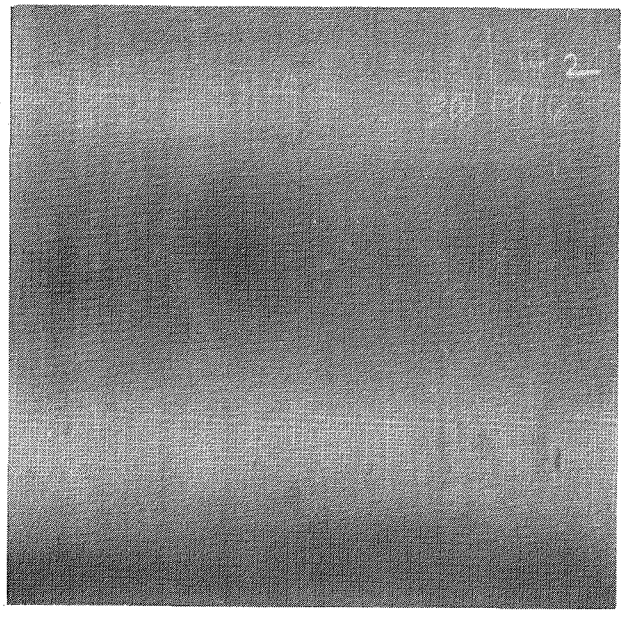
Panel 6B

Panel 7B

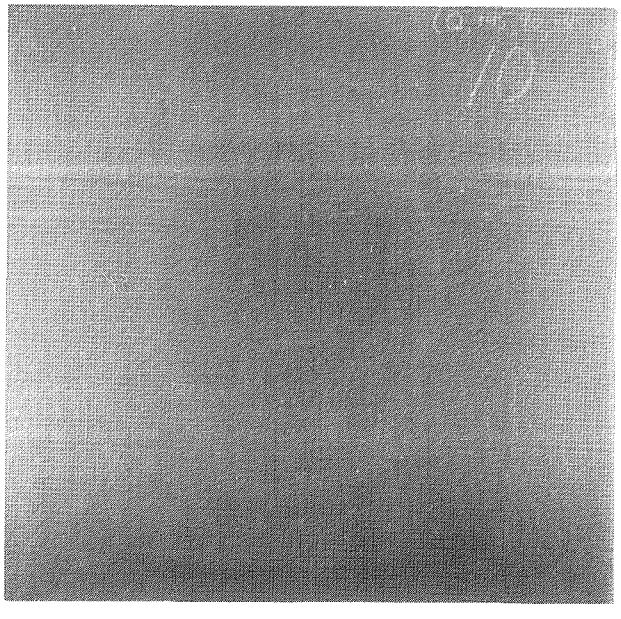


Panel 8B

Figure 14 (Continued)



Panel 9B



Panel 10

Figure 14 (Continued)

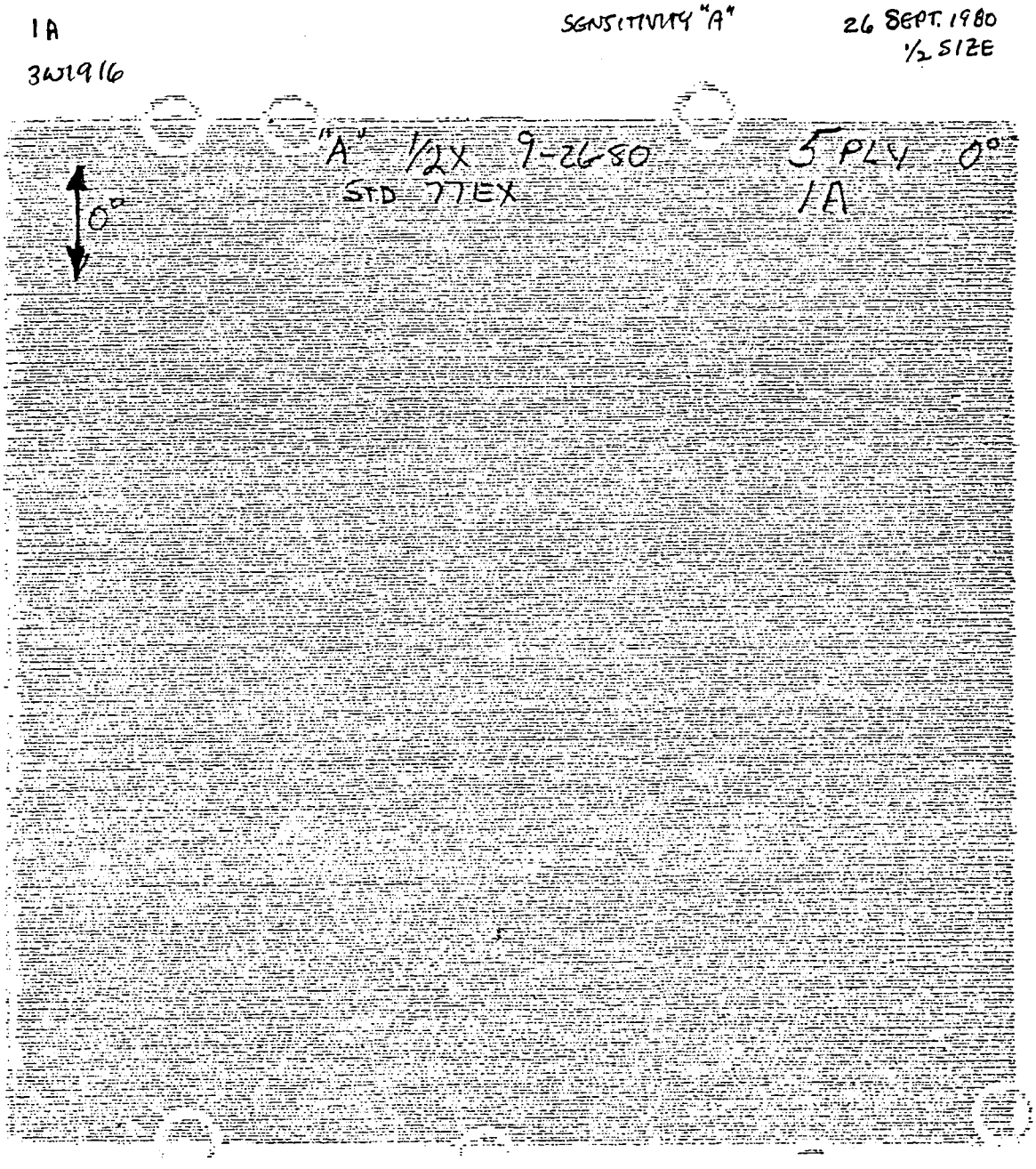


Figure 15

C-Scans on 30x30 cm. (12x12 in.) PMR-15 Laminates
Prepared Using Resco RS17E Porous Tooling

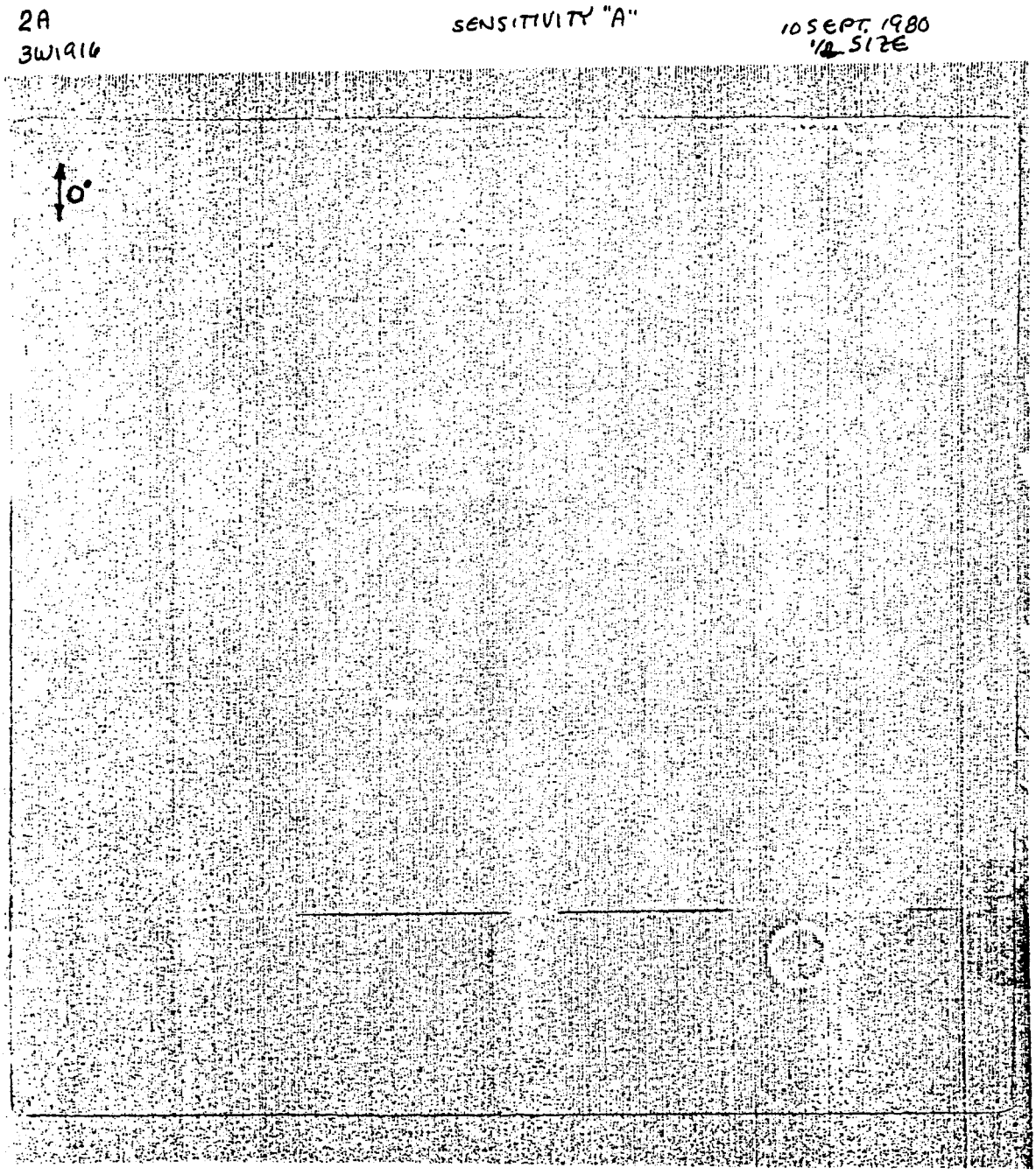
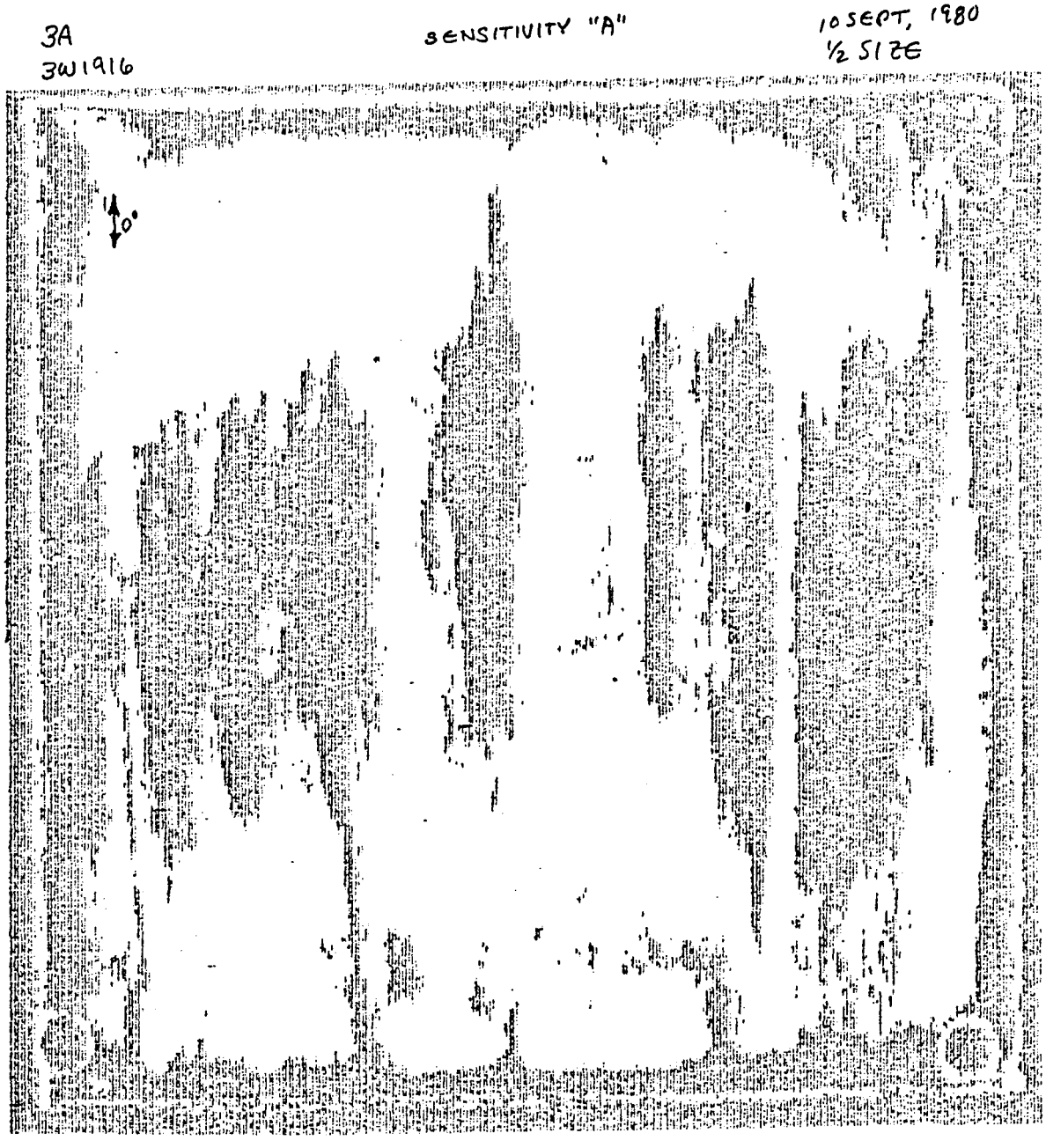


Figure 15 (Continued)



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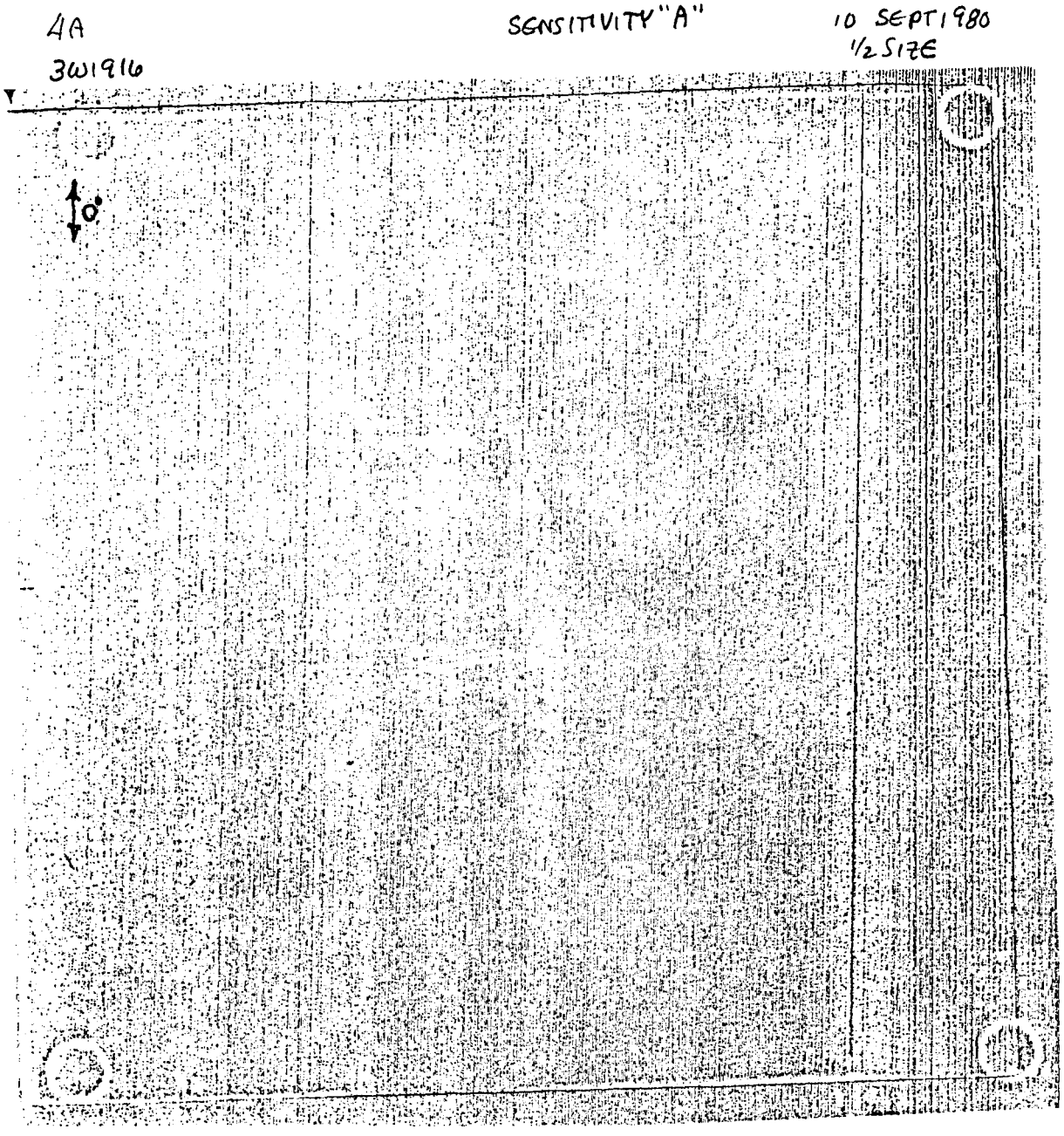

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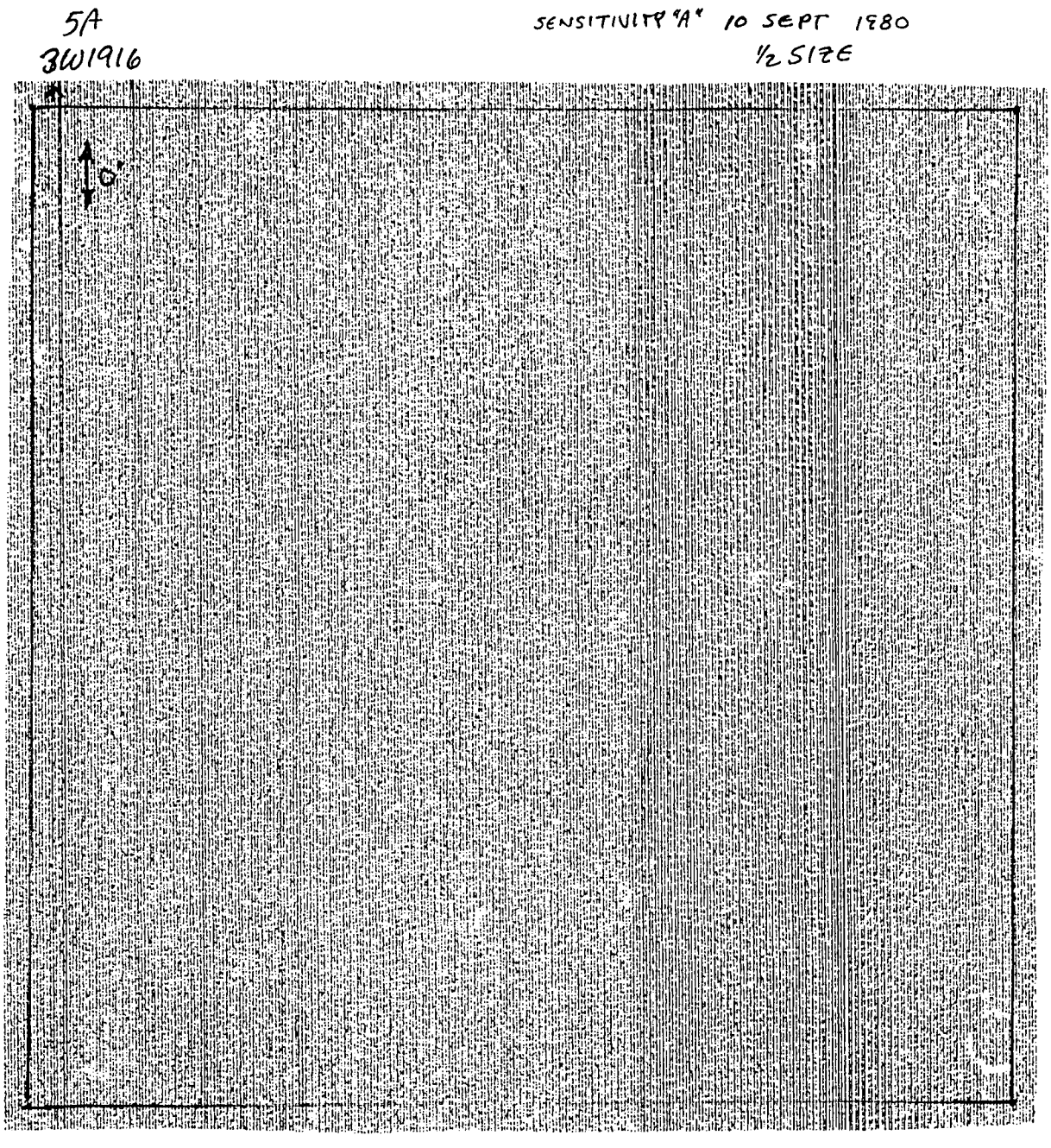

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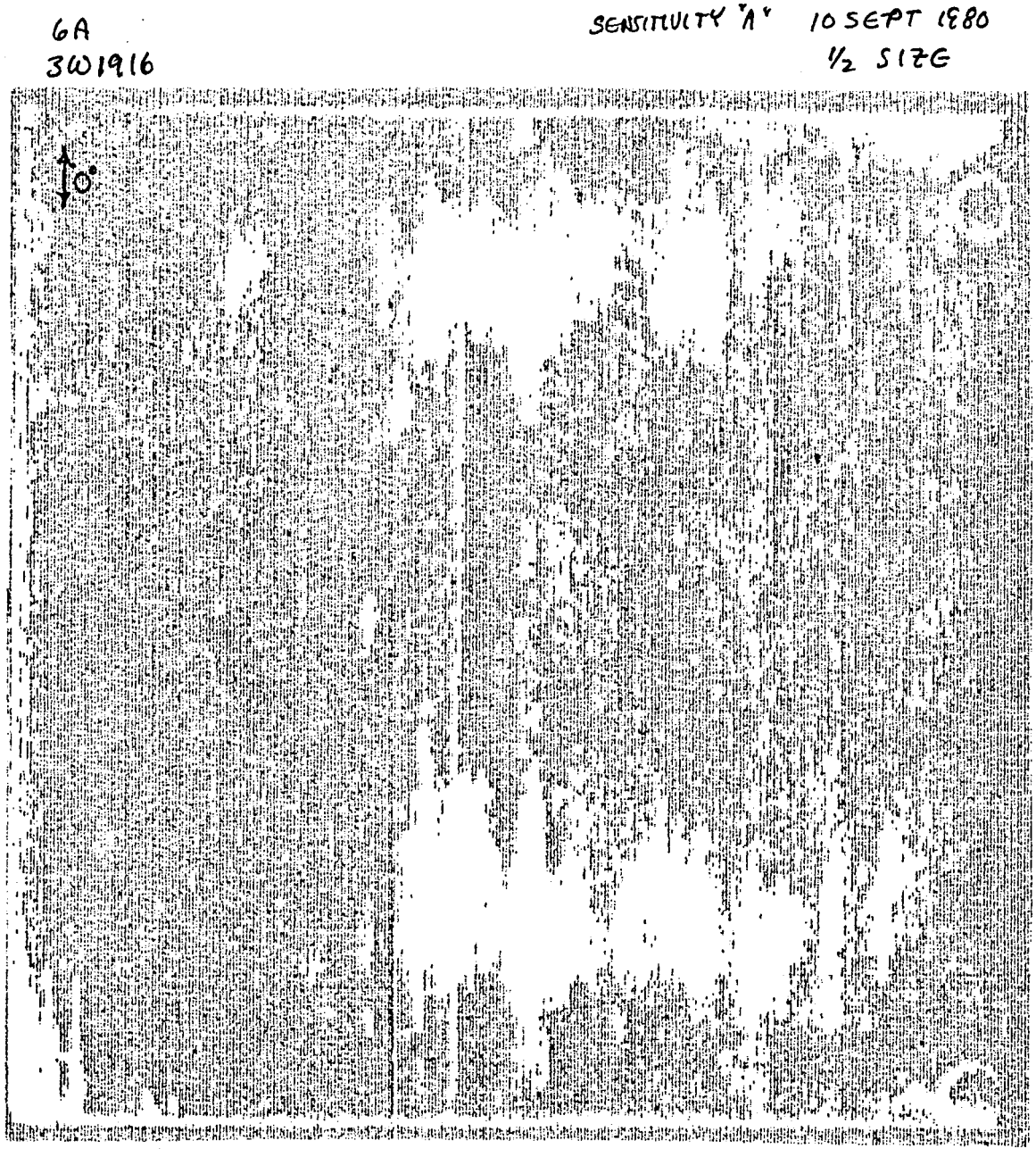

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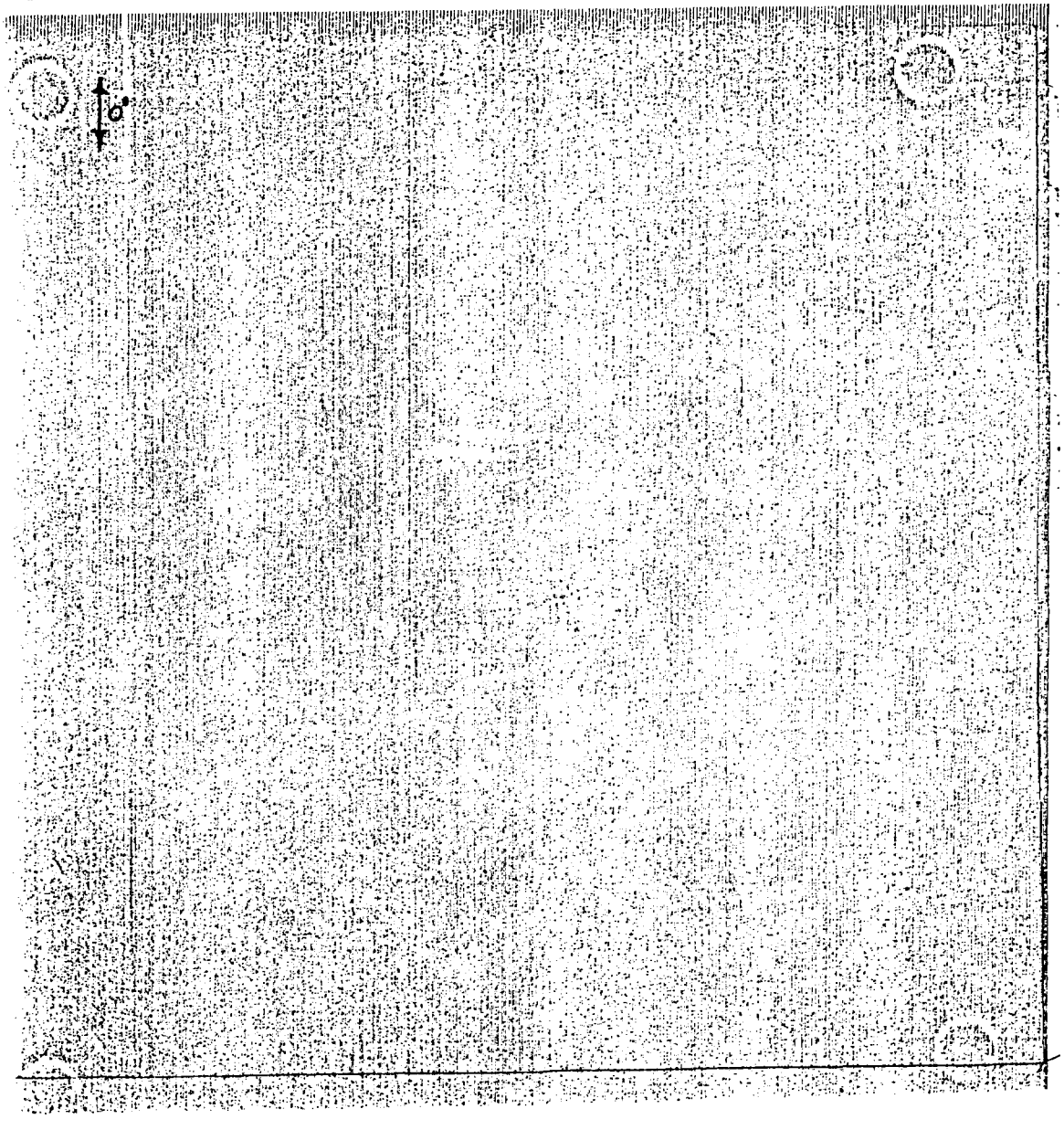

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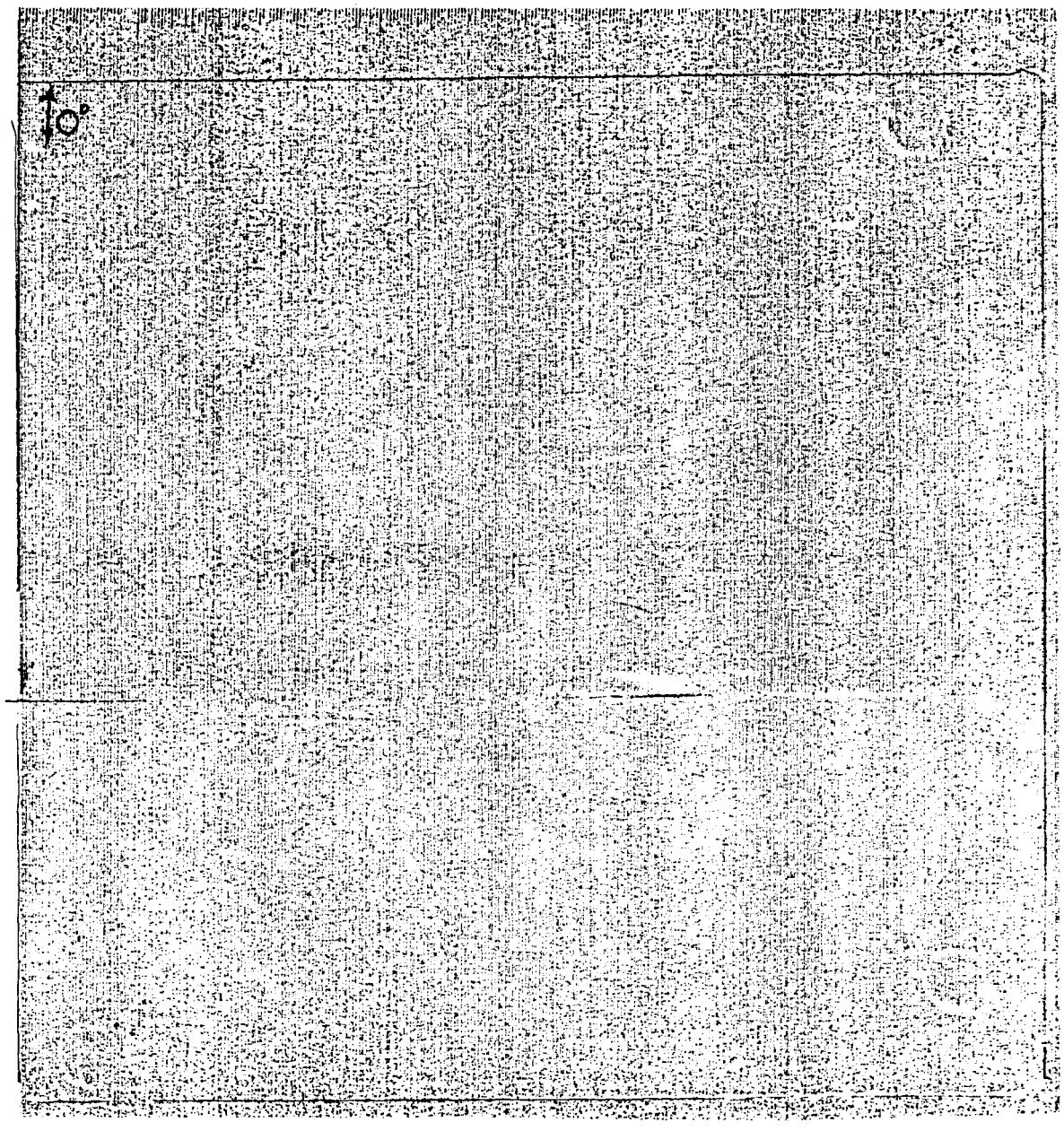

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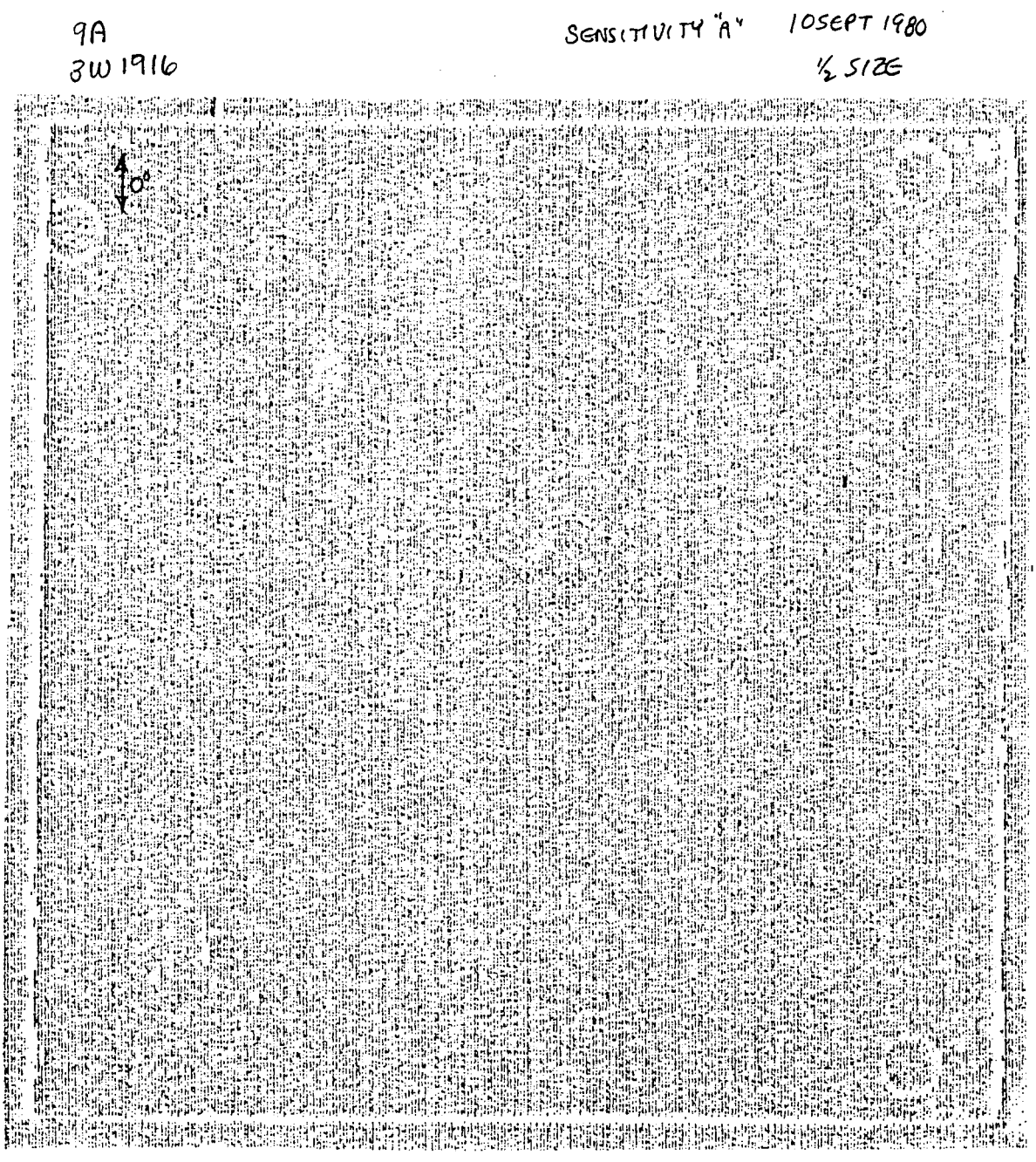

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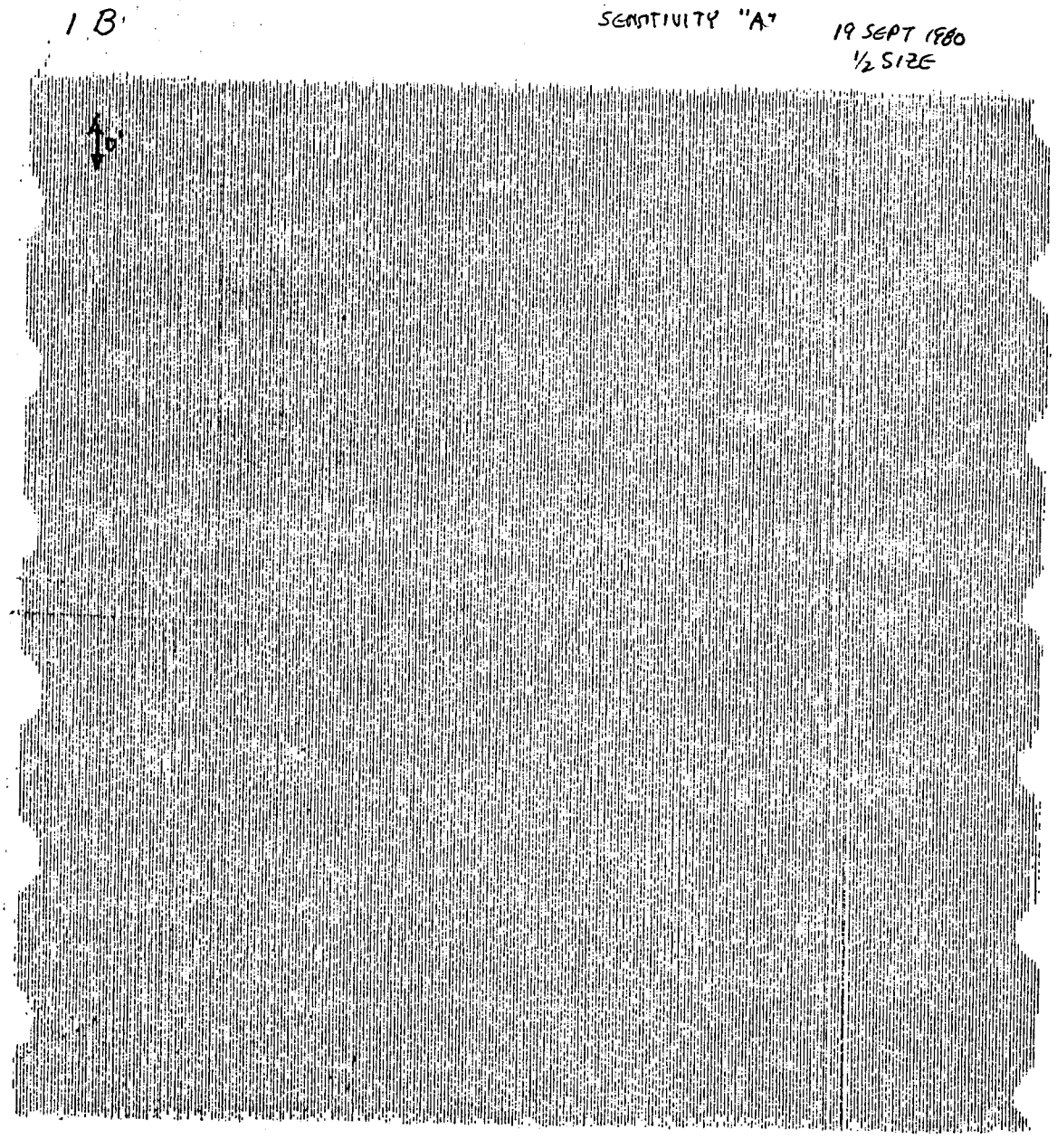

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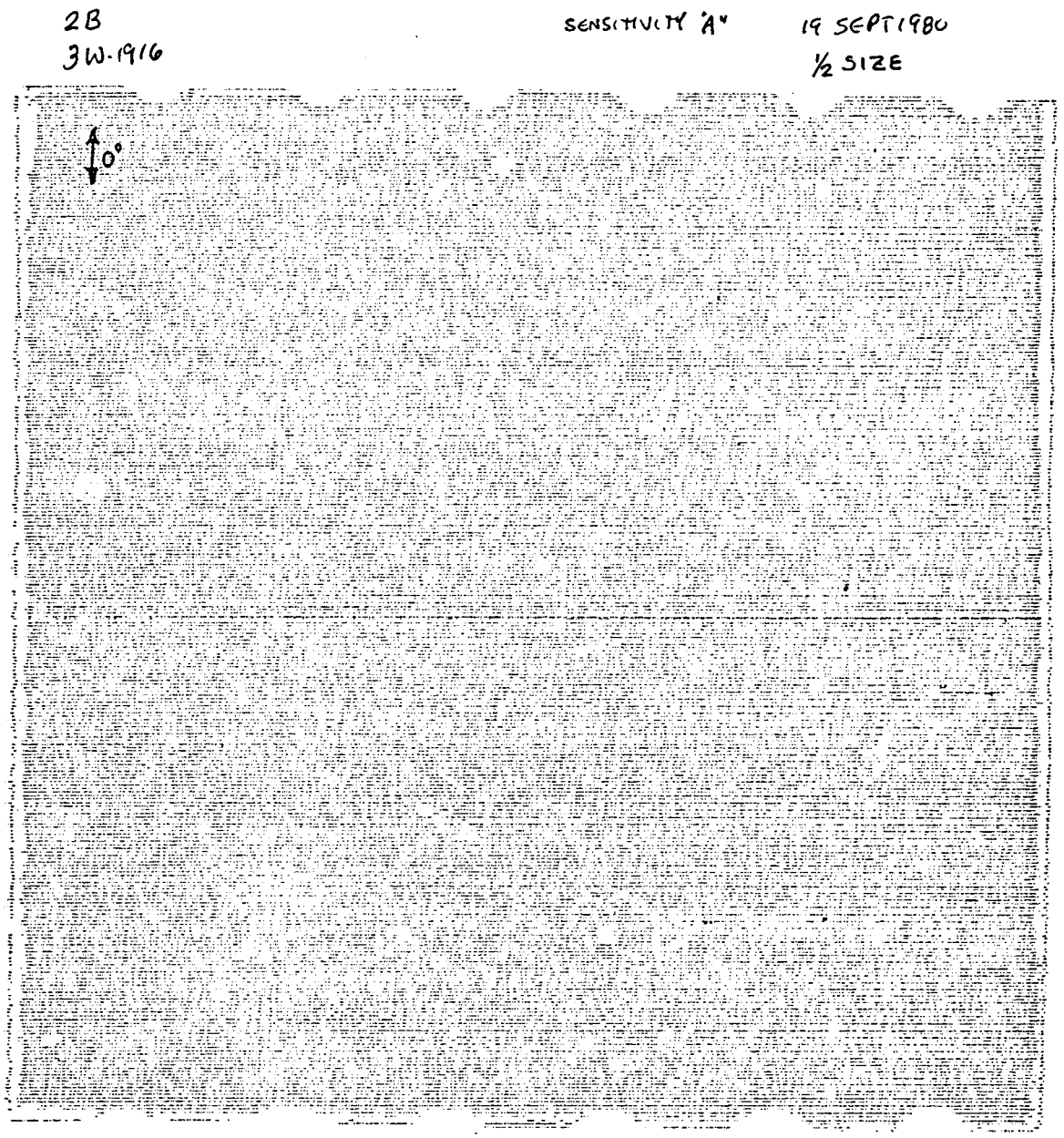

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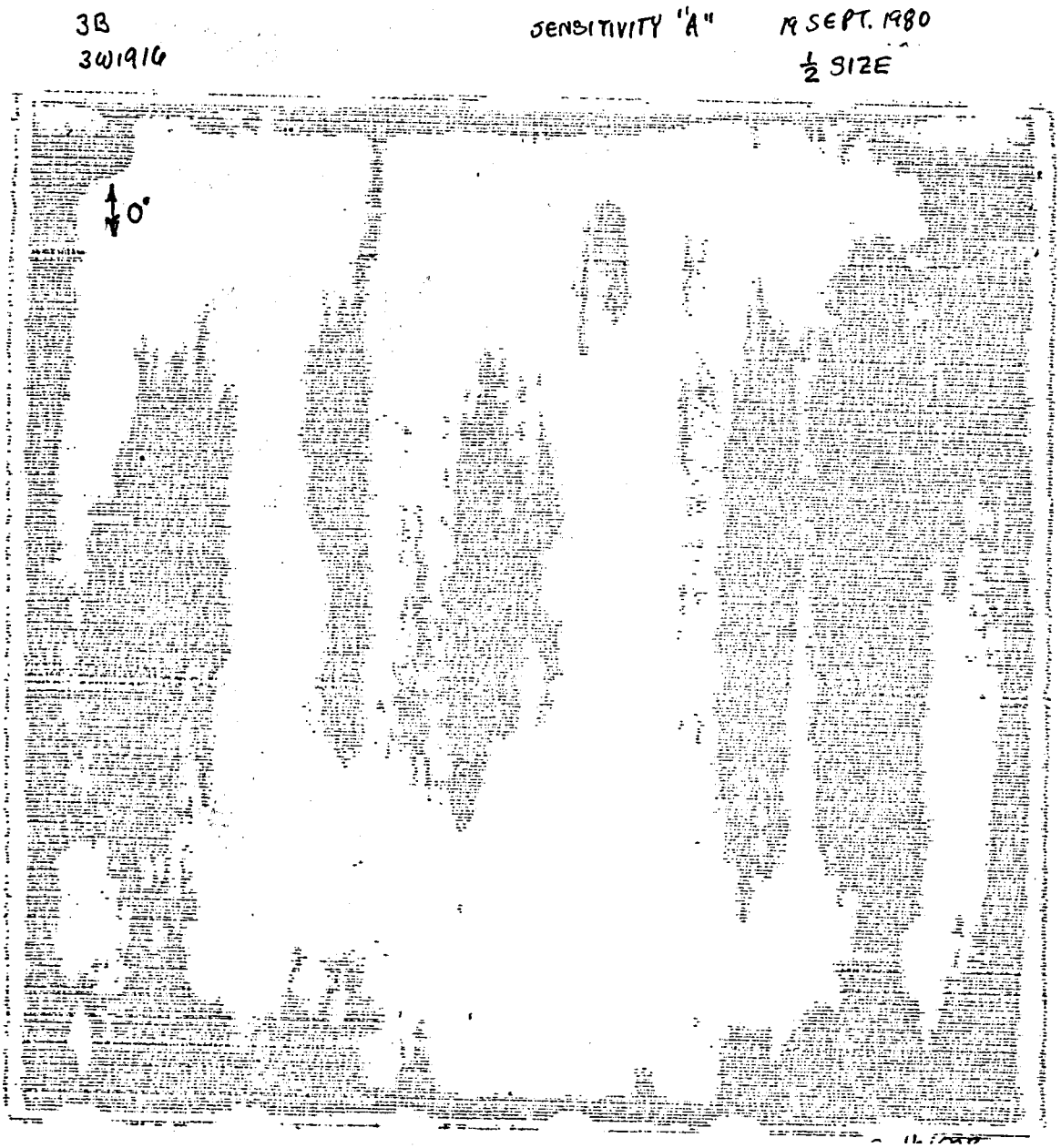

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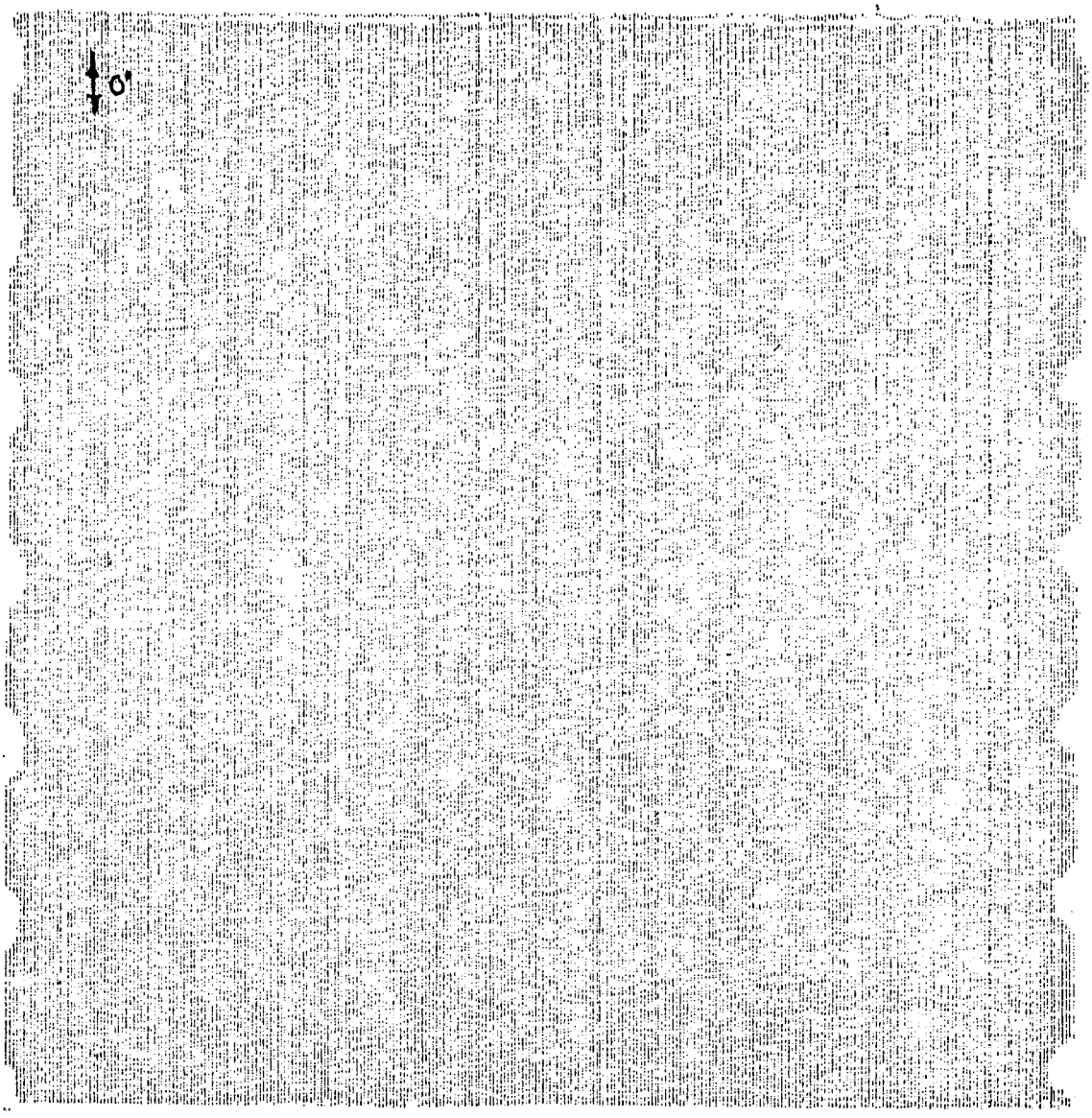

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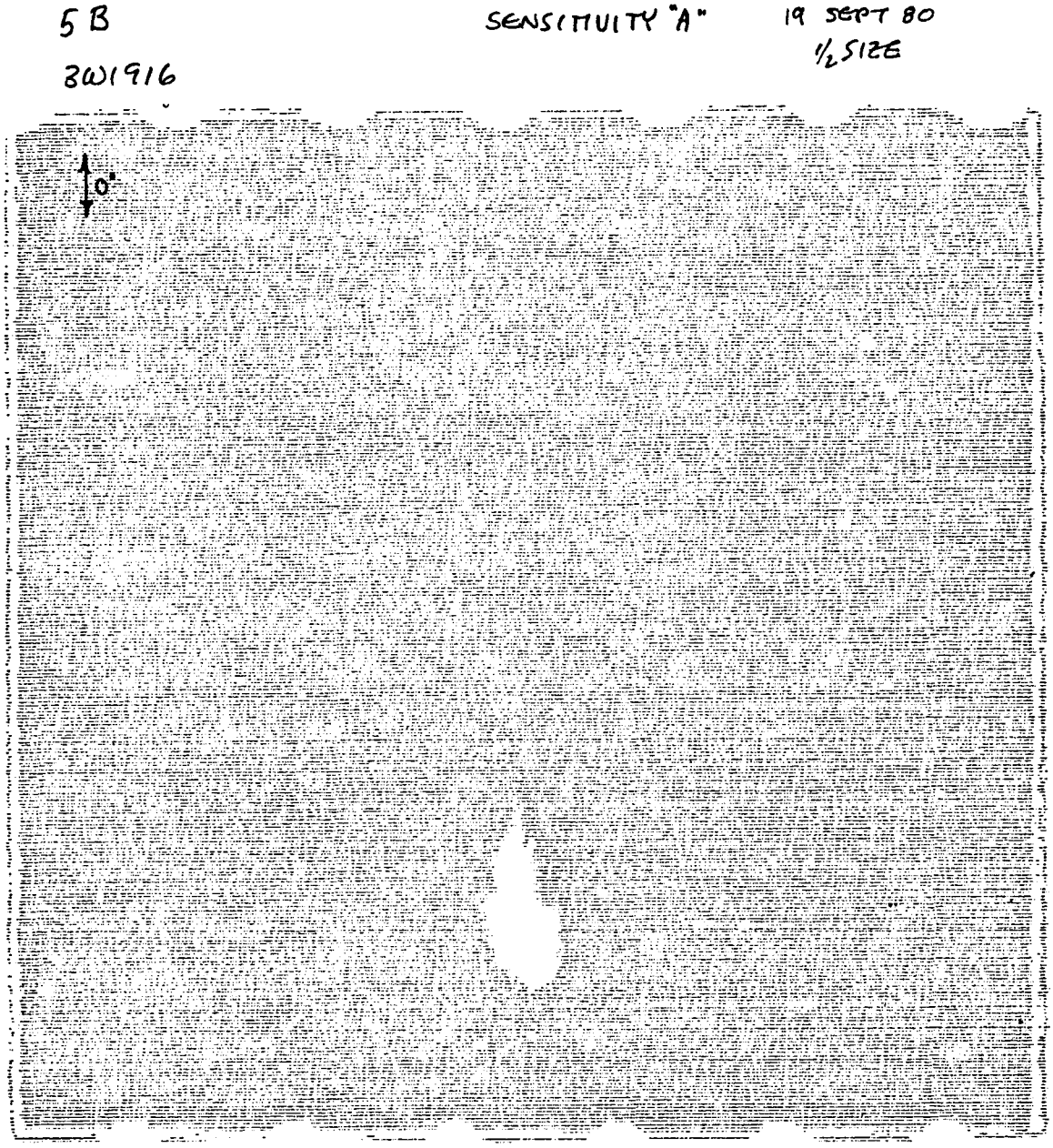

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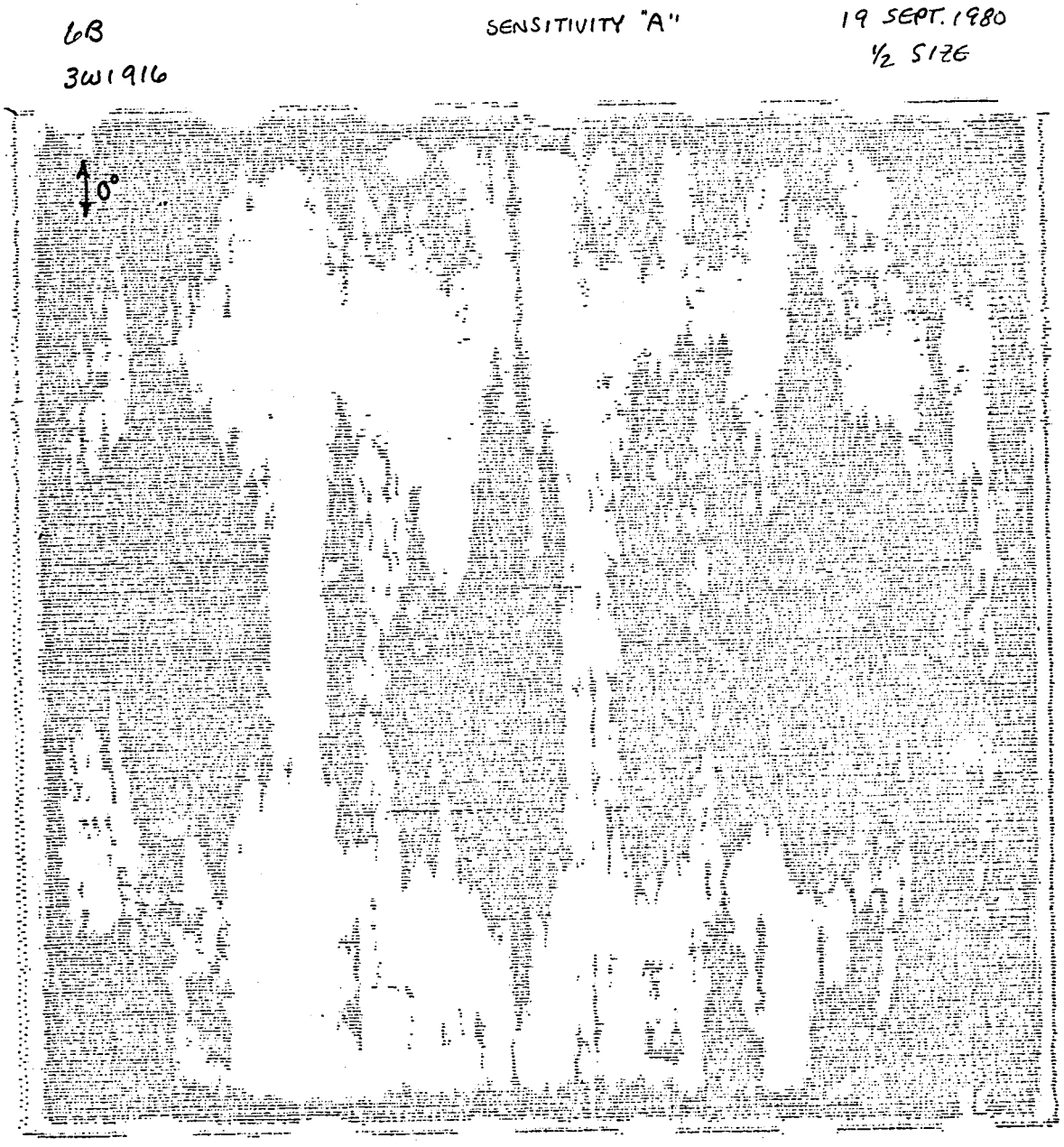

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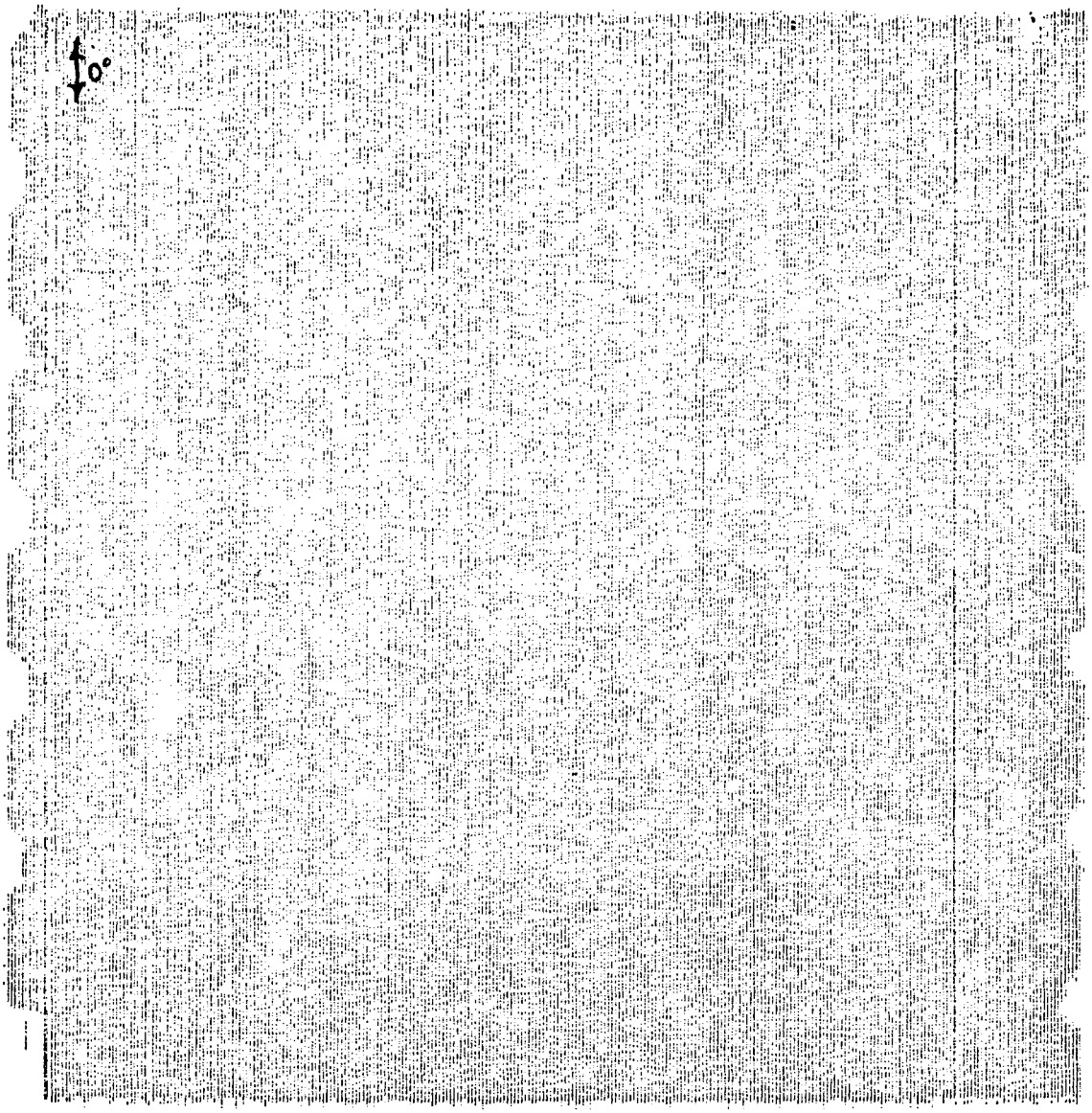

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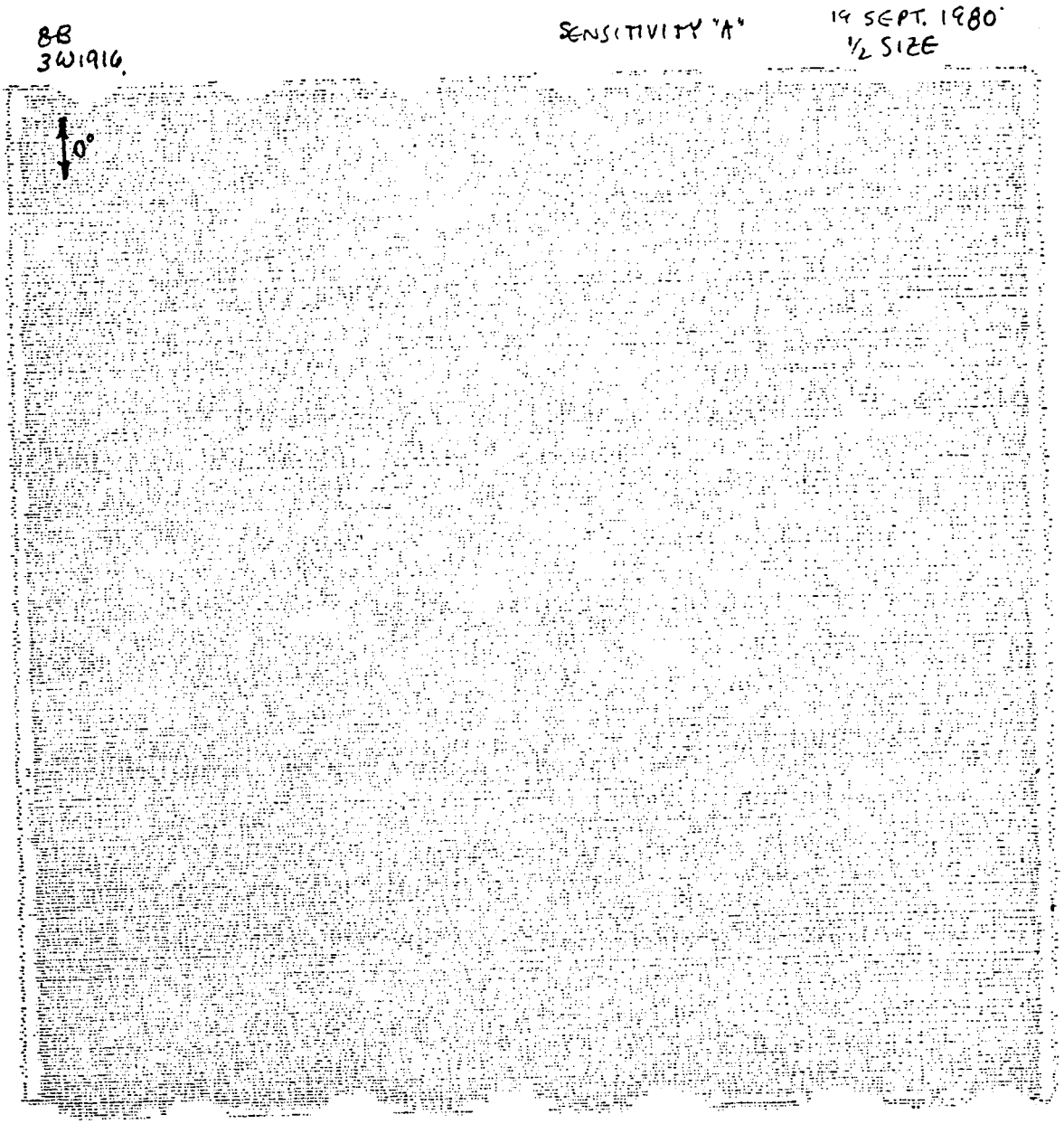

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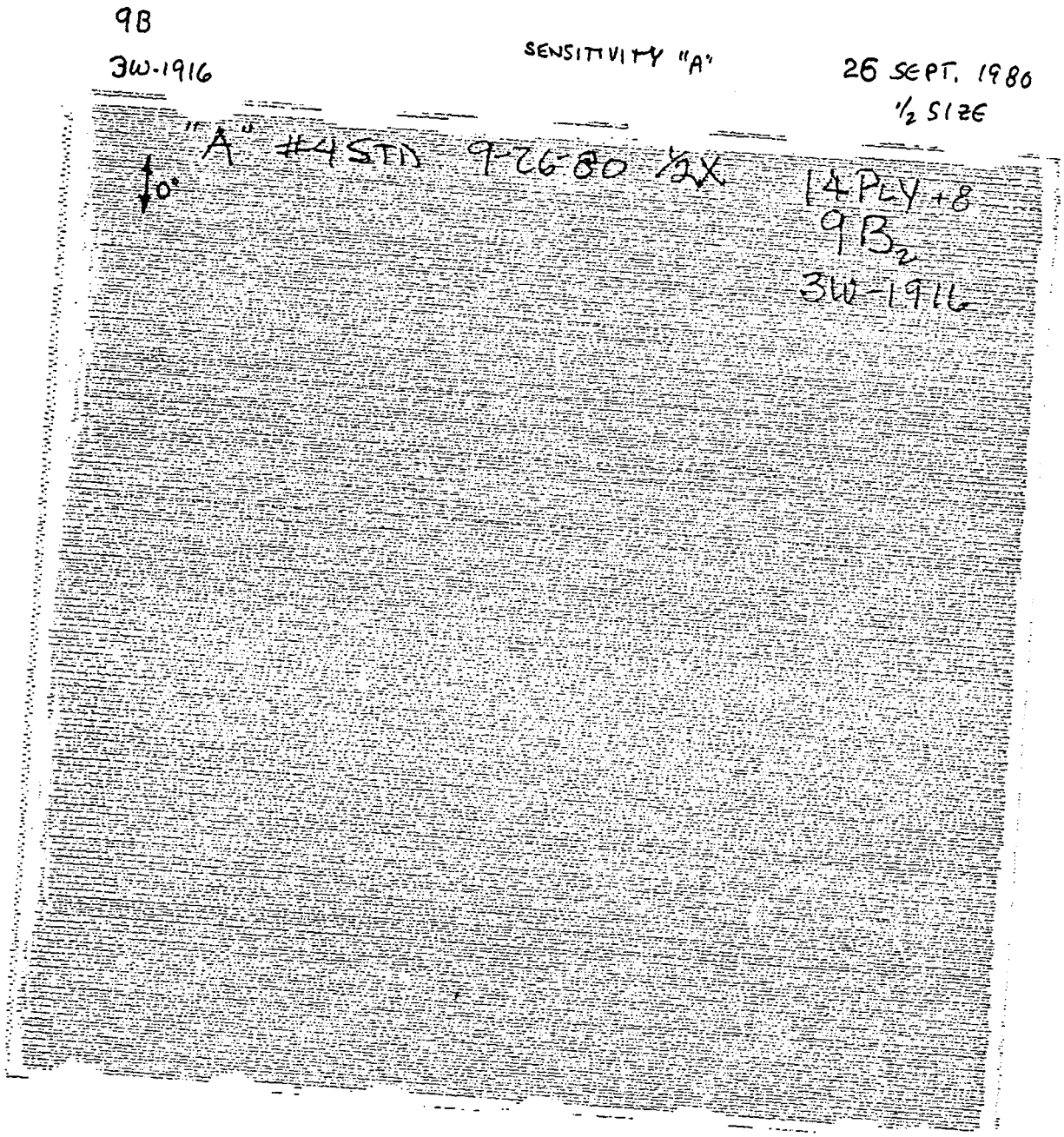

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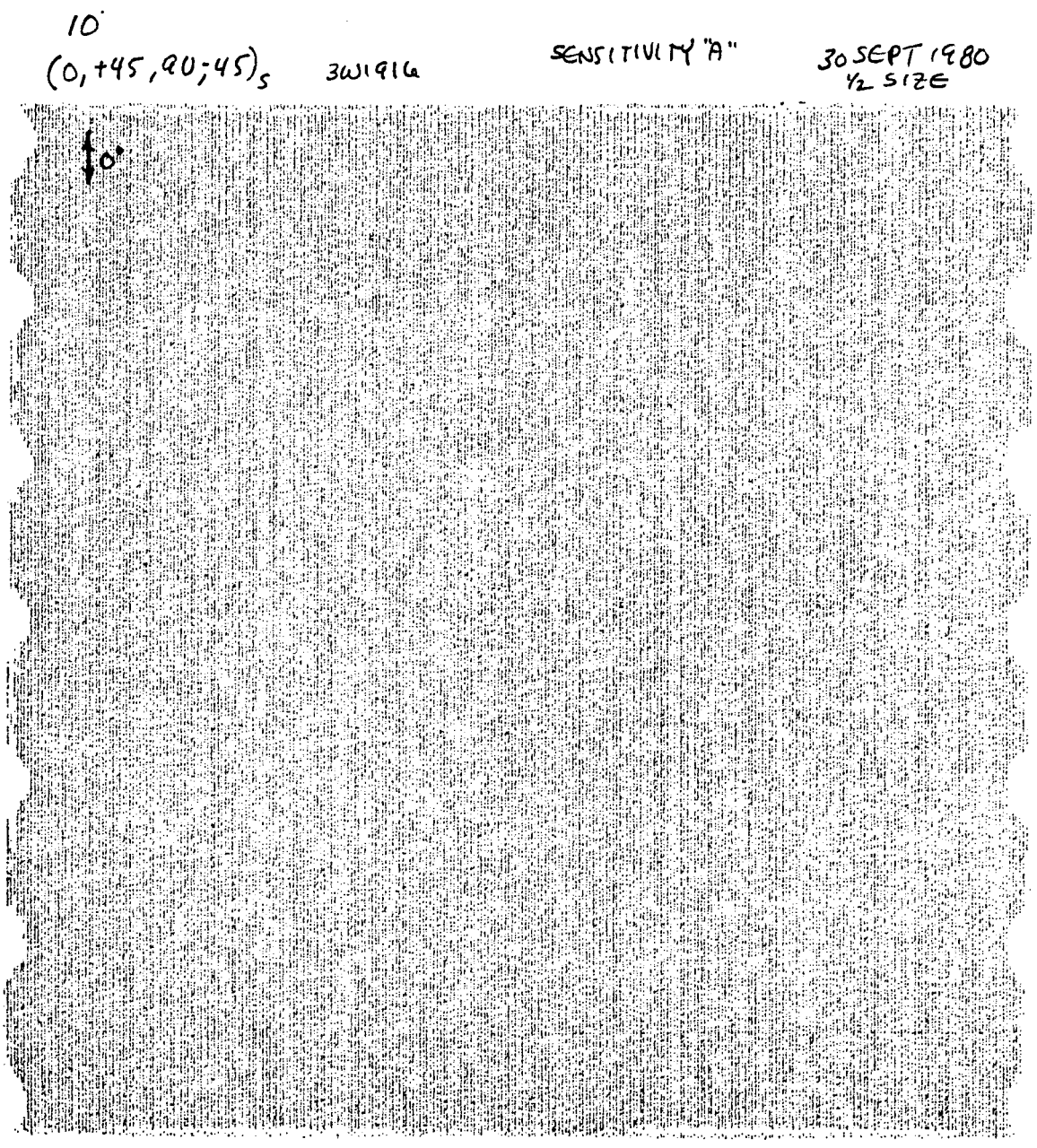

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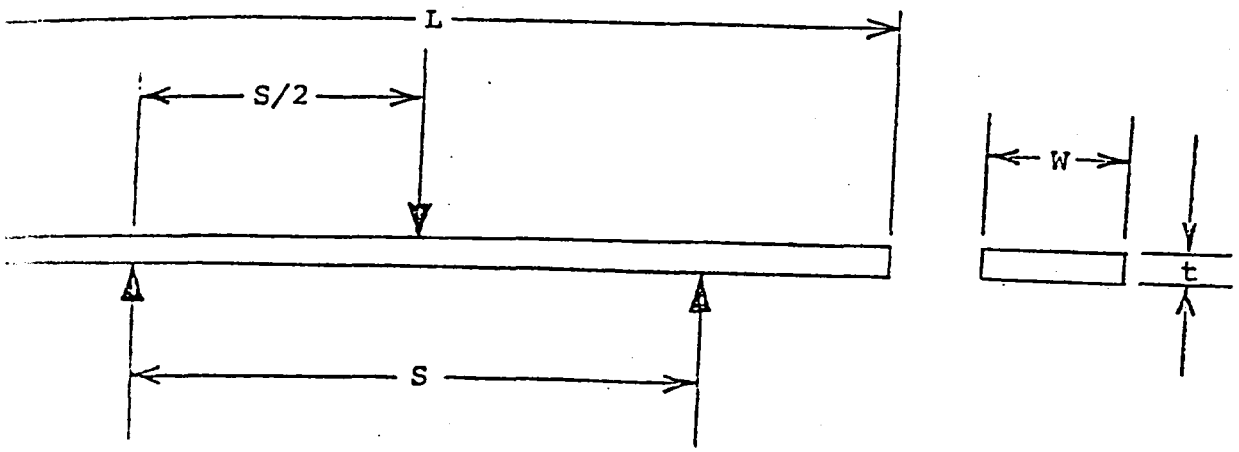


SPECIMEN DIMENSIONS

LENGTH (L) = 10.2 cm. (4.0 in.)

WIDTH (W) = 1.27 cm. (0.500 in.)

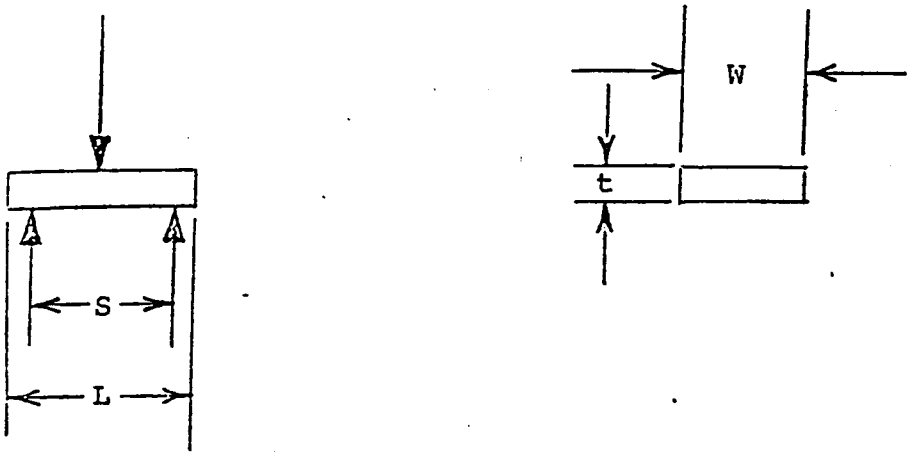
THICKNESS (t) = 0.076-0.32 cm. (0.030-0.125 in.)

FOR t = 0.076 cm (0.030 in.) S = 3.81 cm. (1.50 in.)
t = 0.15 cm (0.060 in.) S = 5.08 cm. (2.00 in.)
t = 0.32 cm. (0.125 in.) S = 7.62 cm. (3.00 in.)

ALL FILAMENTS 0° TO L DIMENSION.

LOAD AND REACTION SUPPORTS ARE 0.64 cm. (0.25 in.) RADIUS STEEL ROD

Figure 16. Longitudinal Flexure Test Specimen



DIMENSIONS

LENGTH (L) = 0.15 cm (0.06 in.) S = 4 x t

WIDTH (W) = 0.64 cm. (0.25 in.)

THICKNESS (t) = 0.15-0.32 cm. (0.060-0.125 in.)

ALL FILAMENTS 0° TO L DIMENSION.

LOAD & REACTION SUPPORTS ARE 0.32 cm. (0.125 in.)

RADIUS STEEL ROD.

Figure 17. Short Beam Shear Test Speciment

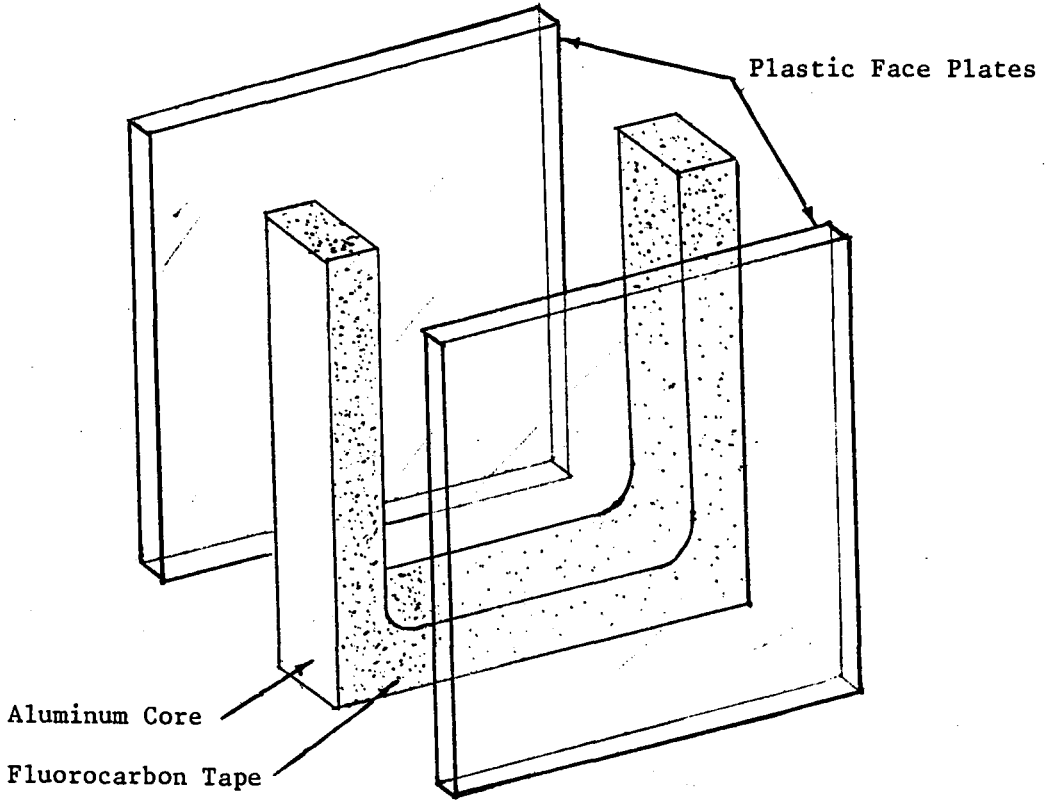


Figure 18. Mold for Scale-Up Tools (Produces 13 x 13 x 1 Inch Tool)

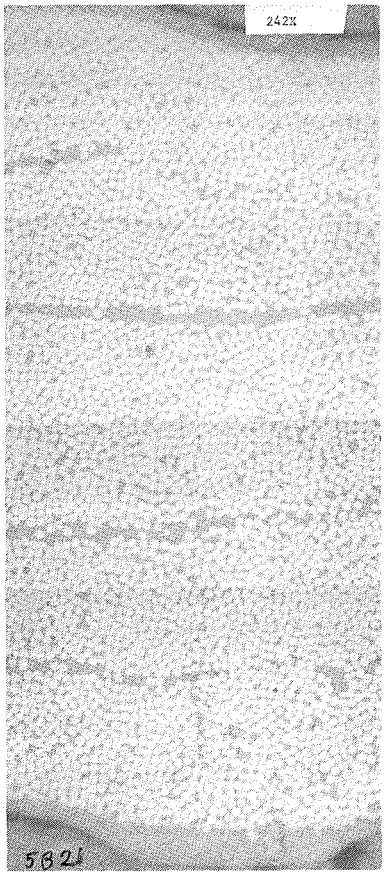


Figure 19. Mosaic Photomicrograph Specimen 5B2, 0°, 5 Ply Laminate Cured on a Porous Tool

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15. Supplementary Notes
Langley Technical Monitor, Robert M. Baucom
Final Report

16. Abstract

A study was conducted to select a porous tooling system for the processing of Graphite/PMR-15 Polyimide laminates in thickness up to 3.2 mm. (0.125 inch). This tool system must have a reasonable strength, permeability dimensional stability, and thermal conductivity to accomplish curing at 600°F and 200 psi autoclave temperature and pressure. A permeability measuring apparatus was constructed and permeability vs. casting water level determined to produce tools at three different permeability levels. On these tools, laminates of 5, 11, and 22 plies (.027, .060, and 0.121 inch) were produced and evaluated by ultrasonic, mechanical, and thermal tests to determine the effect of the tool permeability on the cured laminates. All tools produced acceptable laminates at 5 and 11 plies but only the highest permeability produced acceptable clear ultrasonic C-Scans.

Recommendations are made for future investigations of design geometry, and strengthening techniques for porous ceramic tooling.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Tooling, graphite/polyimide, laminate, porous, ceramic	

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